

TECHNICAL NOTE

D-1944

AN INVESTIGATION OF A NEW NICKEL ALLOY STRENGTHENED

BY DISPERSED THORIA

By Charles R. Manning, Jr., Dick M. Royster,
and David N. Braski

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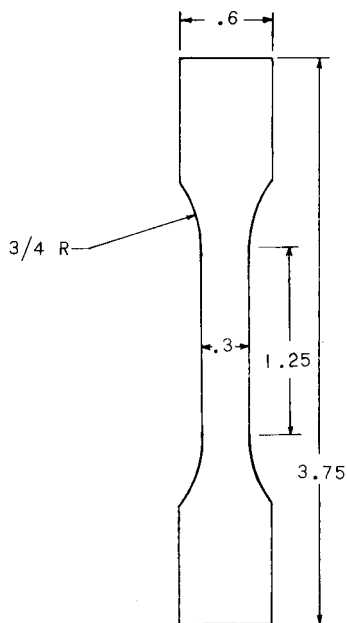
SUMMARY

An experimental investigation was made to evaluate sheet material composed of a new nickel alloy strengthened by dispersed thoria for aerospace applications in the temperature range from 1,800° F to 2,400° F. Mechanical-property tests were made at room and at elevated temperatures from 1,700° F to 2,570° F. The effect of preoxidation at various temperatures on the room-temperature tensile properties is also shown. One diffusion coating was evaluated to determine its effectiveness in reducing oxidation. Fabrication studies included machining, diffusion-bond joining, and several different welding processes. A description of the equipment and procedures utilized in performing the evaluation tests is also included. The metallurgical study included X-ray analysis and a microstructural examination of uncoated and coated sheet material.

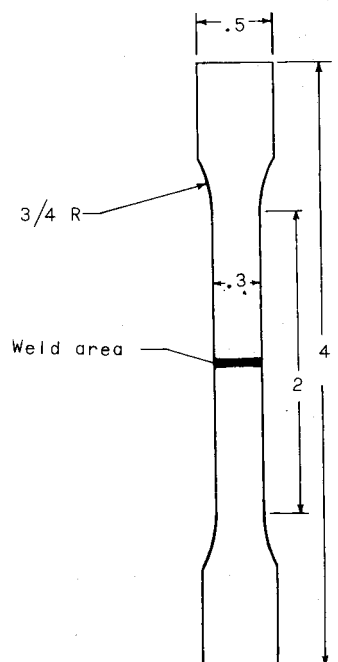
INTRODUCTION

There exists in the aerospace industry a great need for structural sheet alloys which have a combination of strength and oxidation resistance at temperatures above 1,800° F. These alloys should also exhibit properties of creep resistance and relative ease of fabrication. To date the only materials which have exhibited the required properties above 1,800° F are coated refractory alloys, but failure of the coating may cause catastrophic oxidation at the high temperatures involved.

One class of materials which shows promise for providing the required properties in the temperature range from 1,800° F to 2,400° F is that in which a second phase of great stability is uniformly dispersed chemically or mechanically in a nickel matrix. It is postulated that a stable second phase of very tiny particles will block grain boundary and dislocation movements in the matrix material, thereby providing relatively high strength at temperatures which approach the melting temperature of the matrix. A new nickel alloy that is dispersion strengthened with submicron size thoria particles has been developed for structural applications to 2,400° F. This material is reported in reference 1 to exhibit good load-carrying capability and superior oxidation resistance.



(a) Tensile specimen.



(b) Weld specimen.

Figure 1.- Room- and elevated-temperature tensile specimen and weld specimen. All dimensions are in inches.

An investigation was undertaken at the National Aeronautics and Space Administration Langley Research Center to determine the capabilities and limitations of this new dispersion-strengthened nickel sheet material. The study included the determination of tensile properties at room temperature and from 1,700° F to 2,570° F, an investigation of the oxidation properties, as well as X-ray diffraction and microstructure examinations. One diffusion coating was studied to determine whether the oxidation of the nickel alloy could be further reduced. A study of the fabrication characteristics included tungsten-inert-gas, electron-beam, and resistance welding of sheet material. The sheet material was also dimpled and diffusion bonded to form lightweight sandwiches. The results of this investigation are included herein.

MATERIALS AND SPECIMENS

The material used in this investigation included 0.0025-, 0.0040-, 0.010-, 0.025-, and 0.050-inch-thick sheets and a small amount of 1/2-inch and 1-inch-diameter bar stock. The nominal composition of the material is 98-percent nickel and 2-percent thorium by weight. This material was furnished by the E. I. du Pont de Nemours & Company and is known commercially as TD-Nickel. The material will hereinafter be called thoriated nickel. The material was produced by chemically depositing a nickel compound around the stable thorium oxide (thoria) particles, reducing the nickel compound to nickel, compacting into a billet, and then sintering the billet in a reducing atmosphere. The final steps include extruding and rolling the material to the desired thickness. The material and the process used in its manufacturing are described in reference 2.

The dimensions of tensile specimens used in this investigation are shown in figure 1. The same specimen configuration was found satisfactory for both room- and elevated-temperature tensile testing. The butt-welded tensile specimen is shown in figure 1(b). The bend specimens were 2 inches long, 1/2 inch wide, and either 0.025 or 0.050 inch thick.

Three configurations were used for oxidation specimens in the investigation. The first two configurations, cut from 0.025- and 0.050-inch-thick sheet were (1) the 0.75-inch square specimen, and (2) the tensile specimen (fig. 1). The third configuration was 1/8-inch-thick disks machined from both 1/2- and 1-inch-diameter bar

stock. Some of the first and second types of oxidation specimens were coated with a commercially available calorized coating (ref. 3) to study the compatibility of the material and the coating. The calorized coating is an aluminum diffusion coating normally applied to steel. It is applied in a retort at about 1,700° F by pack cementation methods and is then diffused into the base material.

TEST PROCEDURE

Mechanical Properties

Tensile tests.- Tensile tests were made in a 10,000-pound screw-powered testing machine at a head speed corresponding to a strain rate of 0.005 per minute to the yield stress and at an increased head speed corresponding to a strain rate of 0.05 per minute to failure. In the room-temperature test, the load was recorded autographically against strain. Strain was measured by foil-backed SR-4 type strain gages cemented to both sides of the sheet specimen.

In the elevated-temperature tensile tests, the sheet specimens were resistance heated and held at temperature for approximately 1 minute before testing. Specimen temperatures were measured at the center of the test section with an optical pyrometer; no emittance corrections were made. During the test, measurement of the relative separation of the testing machine heads was recorded autographically against load to provide elevated-temperature stress-extension data. The yield point on the stress-extension curves was selected as 0.002-inch offset.

Bend tests.- Bend tests were made in the same 10,000-pound-capacity screw-powered testing machine by using the fixture shown in figure 2. The bend specimens were simply supported on

1/16-inch-diameter pins $1\frac{1}{2}$ inches apart

and were centrally loaded by a ram having a contact radius of 1/8 inch. Bending loads were applied at a head speed of 0.01 inch per minute. During the bend tests made below room temperature, the specimen and fixture were placed in various baths of cold water, ice and water, dry ice and acetone, or liquid nitrogen depending upon the temperature desired. In the low-temperature test, the specimen temperature was



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Figure 2.- Test fixture for determination of bend-transition temperature.

monitored by a mercury-in-glass thermometer to -110° F. When using liquid nitrogen as the coolant, the specimen and fixture were immersed in the boiling liquid for 3 minutes before testing to insure that the specimen temperature was -320° F.

Oxidation Tests

Oxidation tests were made at both normal atmospheric and reduced pressures. The oxidation tests at normal atmospheric conditions were made in static air in a vertical tube furnace equipped with a continuous weighting system. The low-pressure oxidation test was also made in static air in a vertical tube furnace. The furnace tube and weighing system were maintained at a pressure of 1 mm of mercury during this test.

The oxidation testing equipment for the atmospheric-pressure oxidation testing is shown in figure 3. The specimens were suspended on a platinum wire

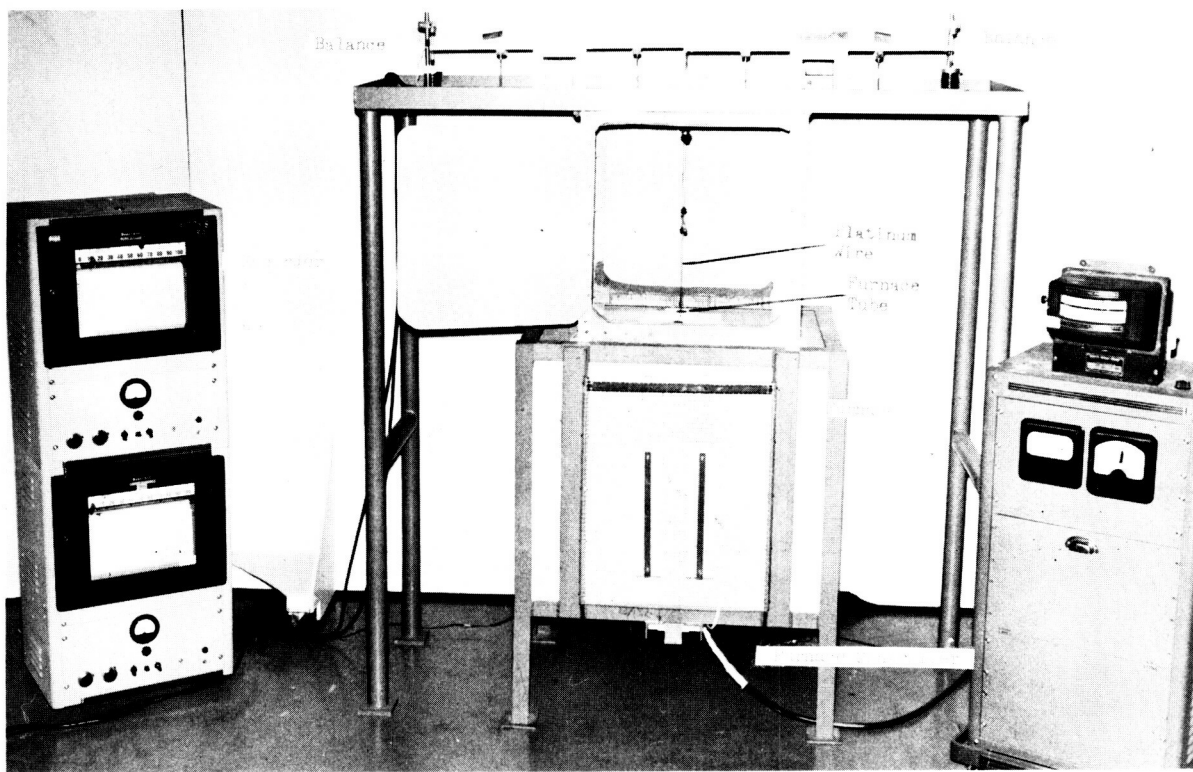


Figure 3.- Balance and furnace setup for static oxidation tests.

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in the furnace and the weight change was autographically recorded by a sensitive balancing system. To check the balance record, all specimens were weighed before and after testing. Test time varied from 24 hours to 285 hours over the temperature range of $1,800^{\circ}$ F to $2,400^{\circ}$ F. The specimens were sectioned after testing and thickness measurements were made by using a filar micrometer stage on a bench

microscope at a magnification of approximately $\times 150$. The micrometer stage was calibrated by using a ruled grating. Each measurement reported represents an average of at least five readings on each specimen.

The test procedure and equipment for the low-pressure oxidation tests are essentially the same as those for the atmospheric-pressure tests except that the balance system is also maintained at 1 mm of pressure.

Metallurgical Studies

Metallurgical studies on the thoriated nickel were made to aid in evaluating the mechanical properties and oxidation tests on coated and uncoated specimens. These studies included X-ray analysis, microstructure examination, and hardness measurements.

X-ray investigation.- Sections were removed from the tested uncoated and coated oxidation specimens as well as from as-received material. The flat faces of these sections were examined by X-ray diffraction in the following manner. The sections were placed in the GE XRD-5 diffractometer and were scanned by using a collimated copper K_{α} X-ray beam with a nickel filter. A scanning angle of 15 to 165 degrees was used and the diffraction pattern was recorded on a strip-chart recorder. The patterns were indexed by using the American Society for Testing Materials (ASTM) card data file.

Similar sections were prepared for X-ray emission studies. The sections were placed in the spectrogoniometer and were scanned by using unfiltered platinum radiation and a LiF analyzing crystal. The amount of thorium present was determined by using a 2-percent standard made from a piece of as-received thoriated nickel.

Microstructure examination.- Sections were removed from the tested uncoated and coated oxidation specimens and from as-received material. The cut edges of these sections were wet ground to remove any cold work left by the cut-off operation. The sections were then mounted and mechanically polished. After polishing, the specimens were etched electrolytically with a solution of 10 grams of oxalic acid in 100 ml of water for 10 to 30 seconds. The etching voltage was 4v to 6v and the amperage was held to less than 0.5 ampere. Photomicrographs were taken at various magnifications from 75 to 1,000 diameters to show the detailed structure in the sectioned specimens.

Hardness measurements.- Hardness measurements were made on the coated oxidation sections that had been mounted and polished. All hardness measurements were made on a microhardness tester by using the Knoop indenter with a 100-gram weight.

Fabrication

The fabrication characteristics of thoriated nickel were studied to determine possible difficulties in machining, forming, and joining the material into structural configurations.

The machining studies consisted of the fabrication of high-temperature testing-machine grips. The forming consisted of dimpling thin sheet material for sandwich panels, and the joining included diffusion bonding of sandwich panels, electron-beam welding, tungsten-inert-gas, and resistance welding of sheet material.

The testing-machine grips were machined from 1-inch-diameter bar stock by utilizing moderate cutting speeds and a small end mill for roughing and finishing. The grips were threaded at very low speeds to eliminate tearing the material.

The dimpling of the 0.0025- and 0.025-inch-thick sheet material to a depth of 0.110 and 0.180 inch, respectively, was done using a brake die. The dimpled sheets were then placed between flat-face sheets and diffusion bonded into structural sandwich panels. This was accomplished by placing the flat-face sheets and the dimpled center sheets into a heavy stainless-steel retort which had been sprayed with Al_2O_3 to prevent the thoriated nickel from bonding to the stainless

steel. The retort was welded vacuum tight and attached to a large pumping system which maintained a vacuum of 1×10^{-4} mm of mercury or lower during the bonding cycle of 24 hours at 2,025° F.

A short study was initiated to develop adequate welding parameters which utilized tungsten-inert-gas and electron-beam techniques. After butt-welding, the specimens were tested in tension to determine the weld strength. This value was then compared with the strength of the as-received material.

RESULTS AND DISCUSSION

Mechanical Properties

Tensile tests.- The results of the tensile tests of the 0.025- and 0.50-inch-thick thoriated-nickel sheet are presented in tables 1 to 3 and figures 4 to 9. The room-temperature stress-strain curves (fig. 4) show that the yield strength of the thoriated nickel preoxidized at 2,000° F for 24 hours was reduced 10 percent from the room-temperature strength

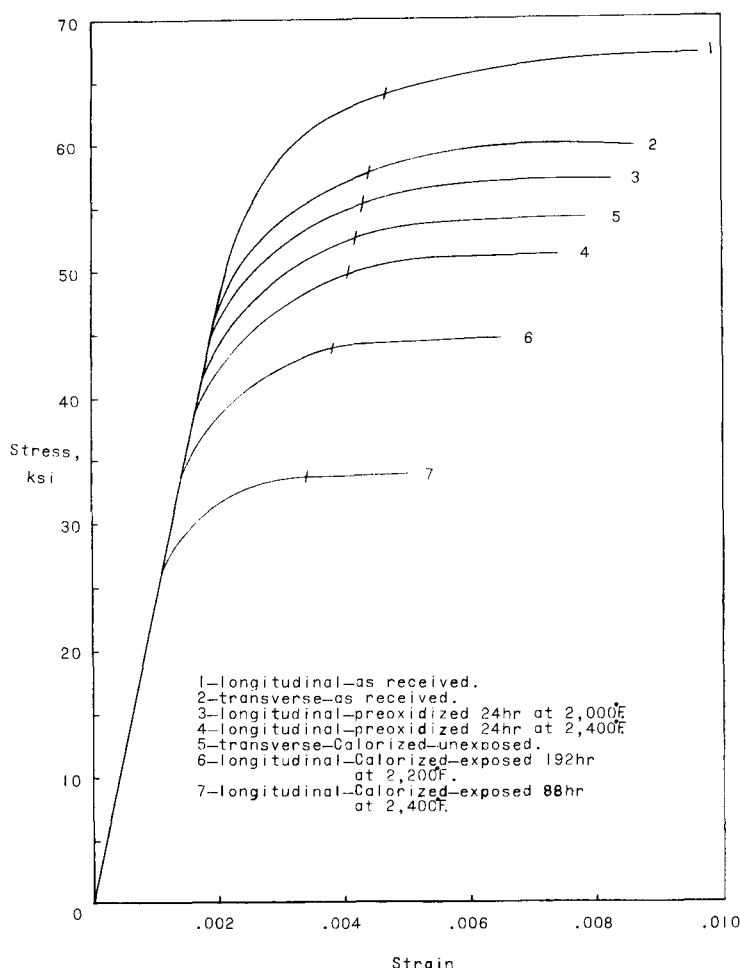


Figure 4.- Tensile stress-strain curves for thoriated-nickel sheet at room temperature.

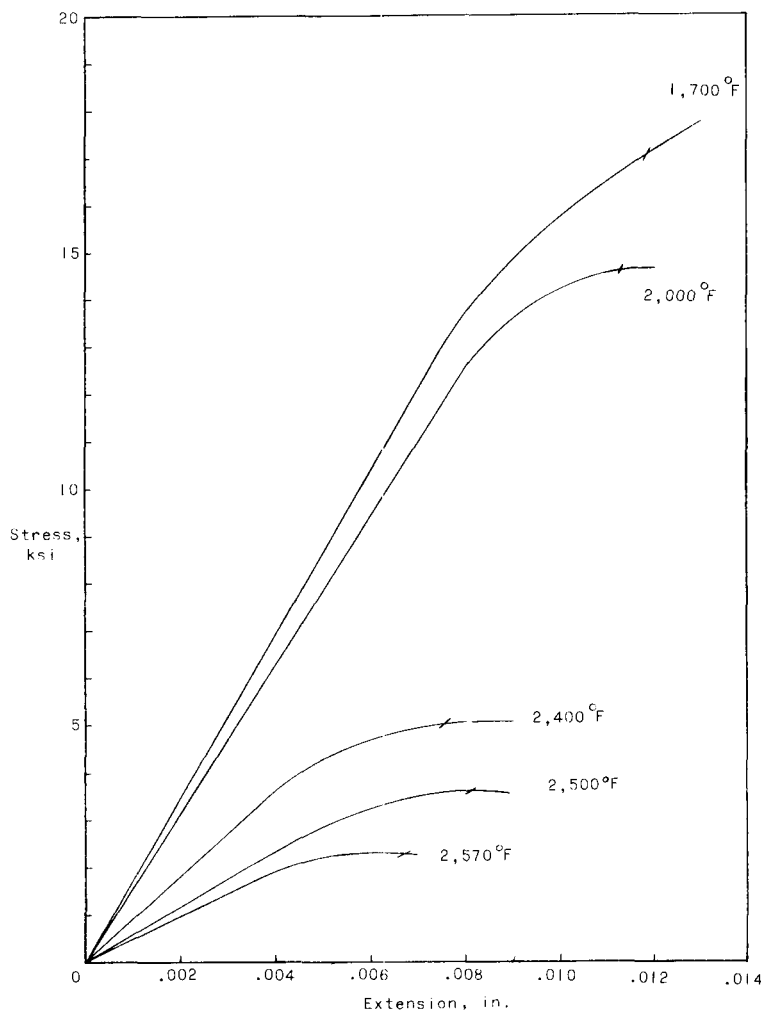


Figure 5.- Stress extension curves for thoriated-nickel sheet at elevated temperature.

Figure 6 also shows that the elongation decreases steadily from the 1,700° F value of 5 percent to 3 percent at 2,570° F. This decrease was demonstrated in the tensile tests made at 2,200° F and above, which showed the specimen exhibited very little reduction in area; no necking was noted at the fracture. Figure 7 shows the effect of preoxidation on the room-temperature elongation of uncoated specimens and also the effect of exposure on the elongation of the coated specimens. Specimens preoxidized at 2,000° F and 2,400° F for 24 hours and tested at room temperature showed only a slight loss in elongation. The specimens that were coated and exposed at 2,200° F and 2,400° F for various times showed some decrease in elongation although the room-temperature elongation always remained above 8 percent. This indicated that the material still remained relatively ductile.

The strength of the thoriated-nickel sheet is compared with that of two superalloys, two refractory alloys, and a chromium composite on a strength-weight

of the as-received sheet, whereas preoxidizing material at 2,400° F for 24 hours caused a loss in strength of about 20 percent. Figure 4 also shows that specimens coated with the aluminum diffusion coating and exposed for 192 hours at 2,200° F have slight losses in tensile strength (see table 1) but that the yield strength decreased approximately 19 percent from the strength of the as-coated material. After 88 hours exposure at 2,400° F the coated specimens had a decrease in yield and tensile strength of 30 to 35 percent. This drop in strength at 2,400° F was partly attributed to a failure of the coating during exposure which caused oxidation to occur.

The results of the elevated-temperature tensile tests are shown in figures 5 and 6. The yield and tensile strength of the alloy was found to be 17.4 and 21.4 ksi, respectively, at 1,700° F. These curves indicate that the material retains usable strength to 2,500° F which is within 150° of the melting temperature of the matrix.

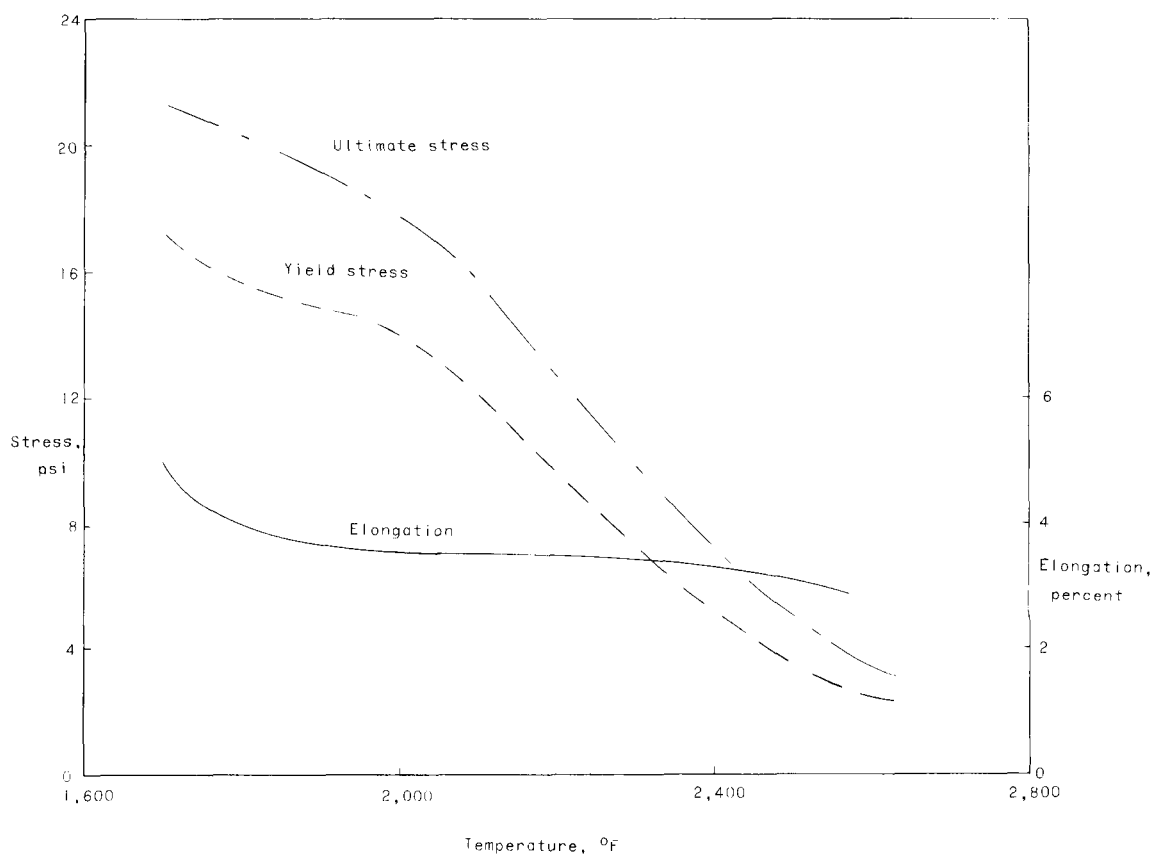


Figure 6.- Mechanical property as a function of temperature for thoriated-nickel sheet.

basis in figure 8. The superalloys used for comparison are René 41, a nickel-base alloy and Haynes alloy no. 25, a cobalt-base alloy; these alloys and the properties thereof are described in references 4 and 5. The refractory alloys used for comparison are Mo-0.5Ti molybdenum alloy (ref. 6) and FS-82 columbium alloy containing 30-percent tantalum (ref. 7). A composite used for comparison was composed of 95-percent chromium and 5-percent magnesium oxide by weight. The properties of this material are given in reference 8.

On a strength-weight basis the thoriated nickel retains a higher strength-weight ratio above 1,700° F and 2,000° F than the cobalt- and nickel-base superalloys, respectively. The strengthening mechanism associated with the thoriated nickel is based on a uniform dispersion of an extremely stable thoria second phase. This stable thoria appears to block grain boundary and dislocation movement to within a few degrees of the melting temperature of the matrix. This allows the material to retain useful tensile properties at temperatures up to 2,400° F for extended time periods. The strengthening mechanism of the nickel-base superalloy (René 41) depends on precipitation hardening as well as solid solution hardening while the cobalt-base superalloy (Haynes alloy no. 25) attains its strength from solid solution hardening. When the superalloys are exposed to temperatures above

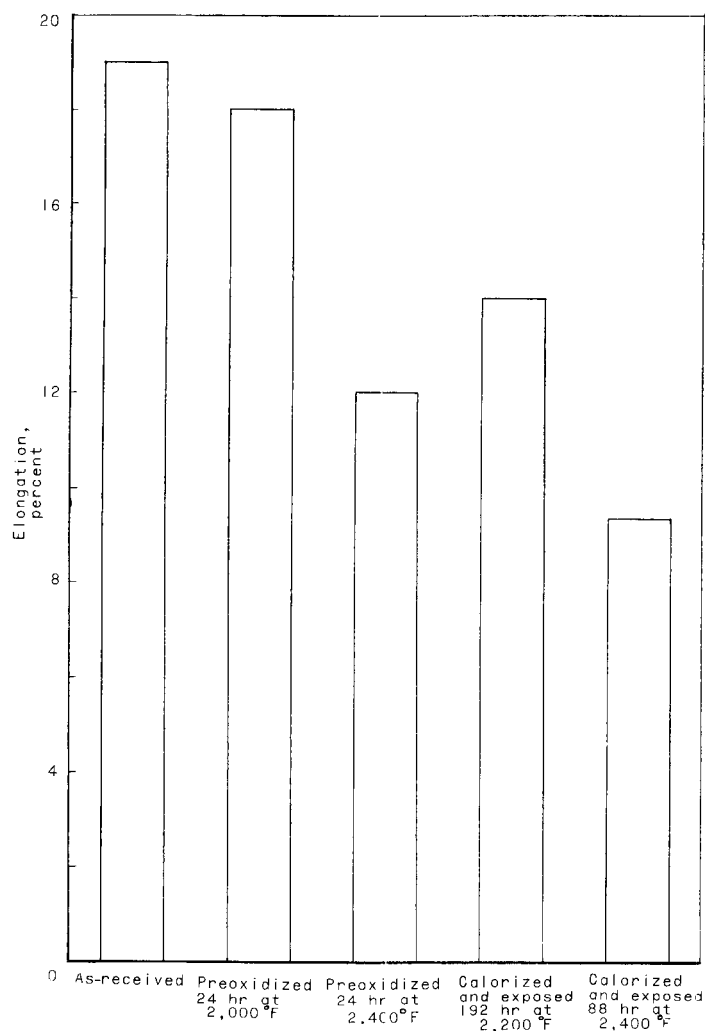


Figure 7.- Room-temperature elongation data for uncoated and coated thoria-nickel sheet exposed at temperatures ranging from 2,000° F to 2,400° F.

2,000° F, the precipitates in the nickel-base superalloy are taken back into solution, and the strengthening from solid solution alloying in both the nickel- and cobalt-base materials decreases because the dislocation mobilities increase. The refractory alloys are considerably stronger than the thoriated nickel in the temperature range from 1,800° F to 2,400° F, but it must be remembered that they require a protective oxidation-resistant coating which may be quite difficult to apply to large sections and complicated configurations. Moreover a sudden failure of the coating on the refractory alloys may cause a catastrophic material failure. The curve for the Cr-MgO composite falls below the thoriated-nickel curve in figure 8 over the entire temperature range. This material has been shown to be affected by nitrogen penetration (ref. 8). The preceding results indicate that the thoriated-nickel alloy should be considered on a strength basis for structural applications which require low stresses in the temperature range of 1,800° F to 2,400° F.

Tensile weld tests.- Table 3 gives the data for the tensile tests made on butt-welded tensile specimens at room temperature. The specimens welded by the electron-beam method as well as

those welded by tungsten-inert-gas (TIG) techniques by using pure nickel filler rod all showed that the weld strength was approximately 80 percent of the as-received material strength at room temperature. Results on the TIG butt-welded specimens with no filler rod showed the strength to be 50 percent of the as-received material strength at room temperature. This low strength using no filler material was due to a very porous weld. Elongations for the electron-beam-welded and TIG welded specimens with no filler rod ran about 2 to 3 percent, whereas TIG welded specimens using filler rod had about 6-percent elongation.

Transition temperature.- Bend-test data are presented in figure 9. An attempt was made to determine bend-transition temperature in this report in the following

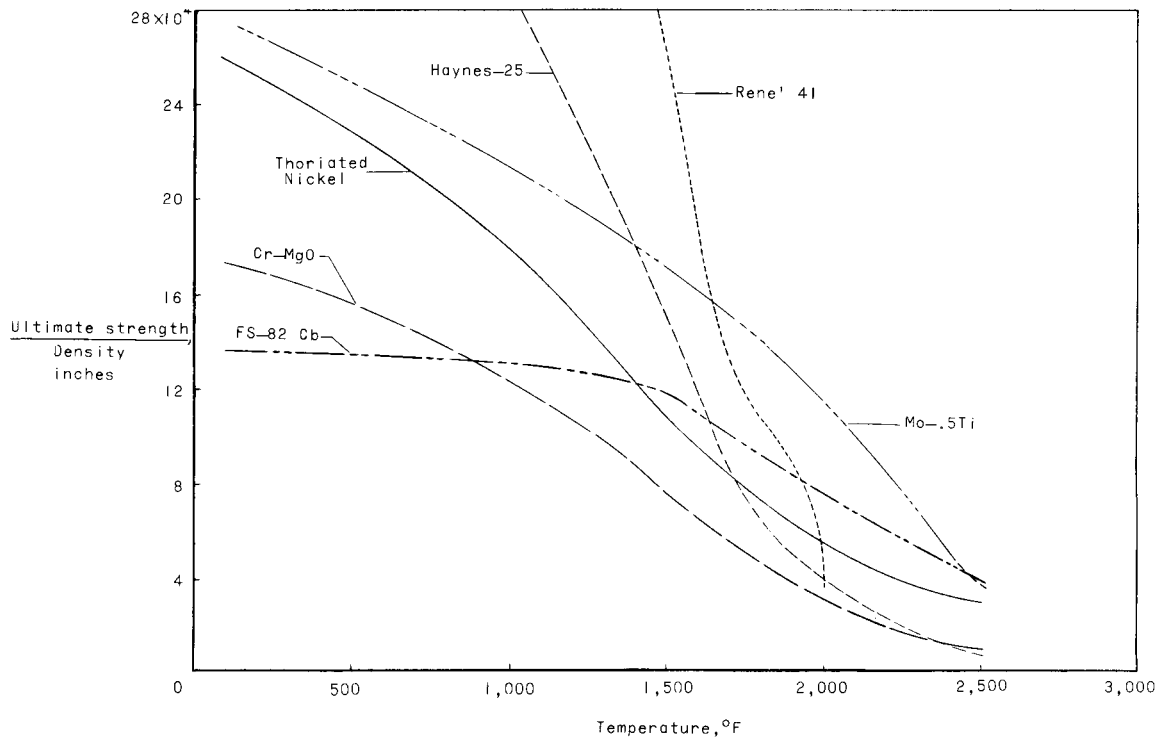


Figure 8.- Comparison of thoriated-nickel sheet with two superalloys, two refractory-metal alloys, and a Cr-MgO composite on a strength-weight basis.

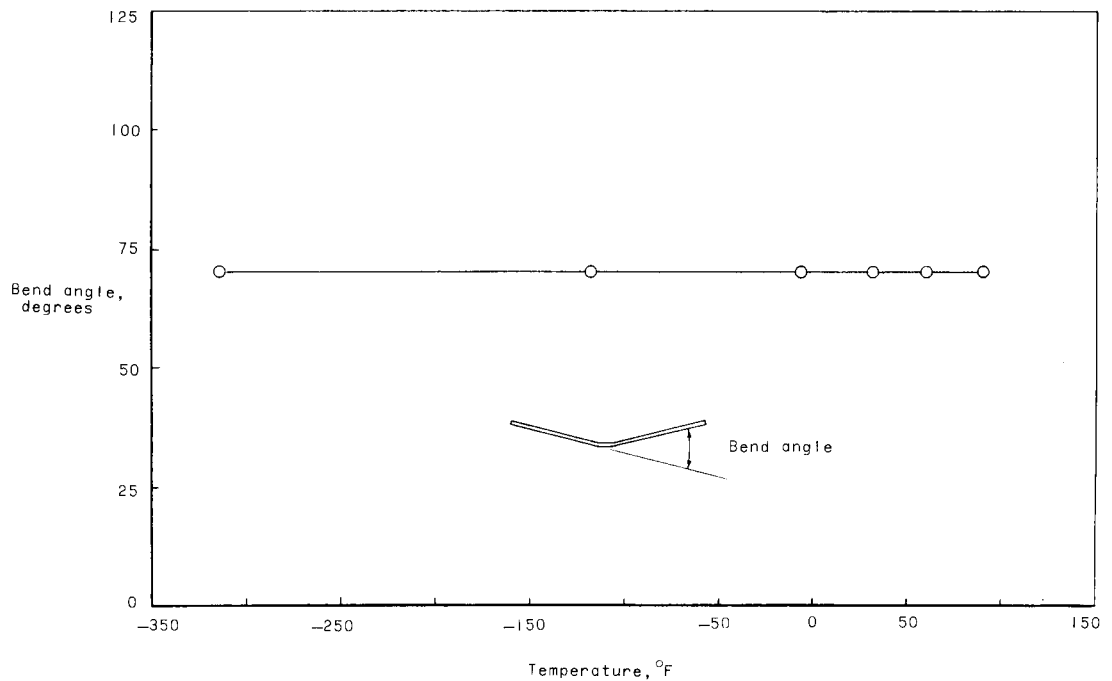


Figure 9.- Curve showing bend ductility for the thoriated-nickel sheet material; sheet thickness, 0.050 inch. Each circle is for a different specimen.

manner. A specimen that withstood a 60° bend as shown in figure 9 without failure was considered to be in the ductile range and one that failed before bending 60° was considered to be brittle. Figure 9 shows that all six specimens tested withstood the maximum bend angle (71°) that the fixture would allow from 100° F to -320° F. Although the transition temperature in bending was not determined, good bend ductility was maintained to -320° F.

Oxidation Properties

Uncoated specimens.— The results of oxidation tests on thoriated-nickel sheet and bar stock are shown in figures 10 to 13. Figure 10 compares curves of weight

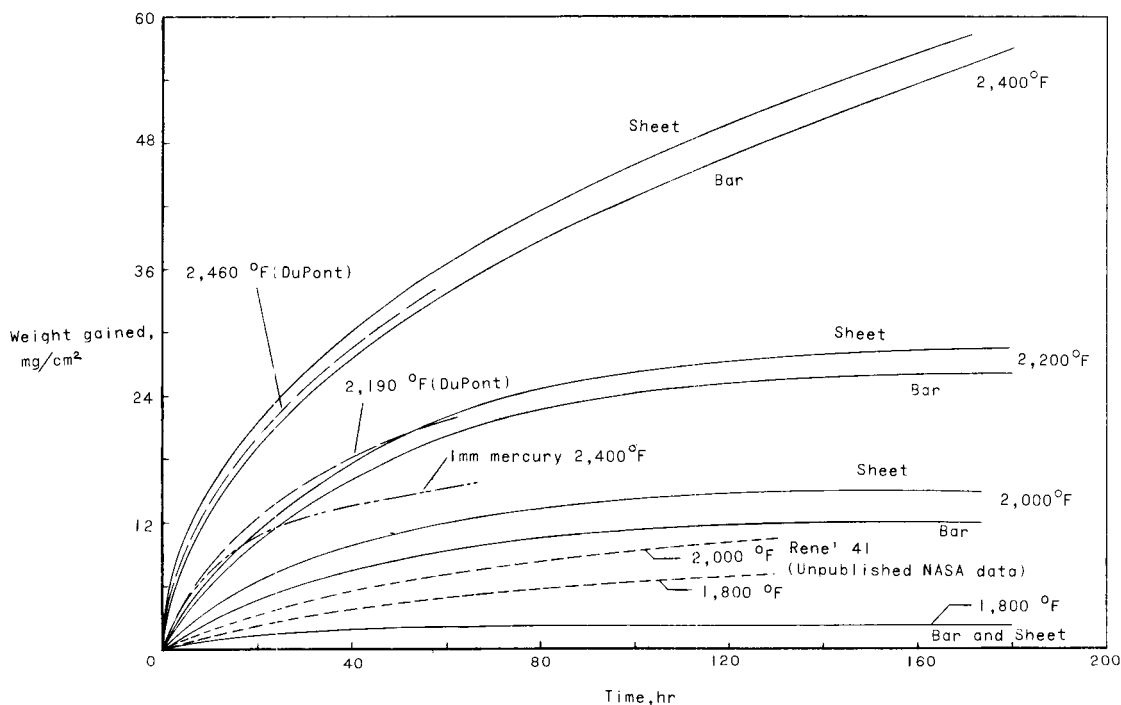


Figure 10.— Oxidation curves for the thoriated-nickel alloy and René 41 showing weight gained per unit area as a function of time.

gained as a function of time at temperatures from $1,800^\circ$ F to $2,400^\circ$ F for thoriated nickel and a superalloy (René 41). The results obtained in this investigation agree with results supplied by E. I. du Pont de Nemours & Company for thoriated nickel. A test made at a pressure of 1 mm of mercury and a temperature of $2,400^\circ$ F (fig. 10) showed the weight gained was reduced from 34 mg/cm^2 at 60 hours for 1 atmosphere to 15.5 mg/cm^2 at 60 hours at the reduced pressure. The unpublished results of oxidation testing of René 41 at $1,800^\circ$ F and $2,000^\circ$ F (fig. 10) indicate that the weight gained per unit area for the René 41 was less than for the thoriated nickel at $2,000^\circ$ F. These results may be misleading in that the oxide attack on the thoriated nickel is a very uniform surface attack which does not adversely affect grain boundaries. The nickel-base René 41 is severely attacked in the grain boundaries (ref. 9) and after exposures at $1,800^\circ$ F and

2,000° F there is a depleted area under the oxide film. This depleted area combined with the intergranular oxide attack reduces its usefulness for long time exposures near 2,000° F.

The oxide formed on the surface of the thoriated nickel was NiO. The outside layer was black and shiny, but the layer near the metal surface was green. A possible explanation for the formation of these types of oxides will be given in the section entitled "Metallurgical Investigation."

Another indication of oxidation resistance of a material is obtained from a determination of the loss of original material to oxide formation. The results of thickness measurements made on the thoriated-nickel sheet after oxidation are presented in figure 11. The amount of original material remaining after oxidation is plotted as a function of exposure time for temperatures of 2,000° F

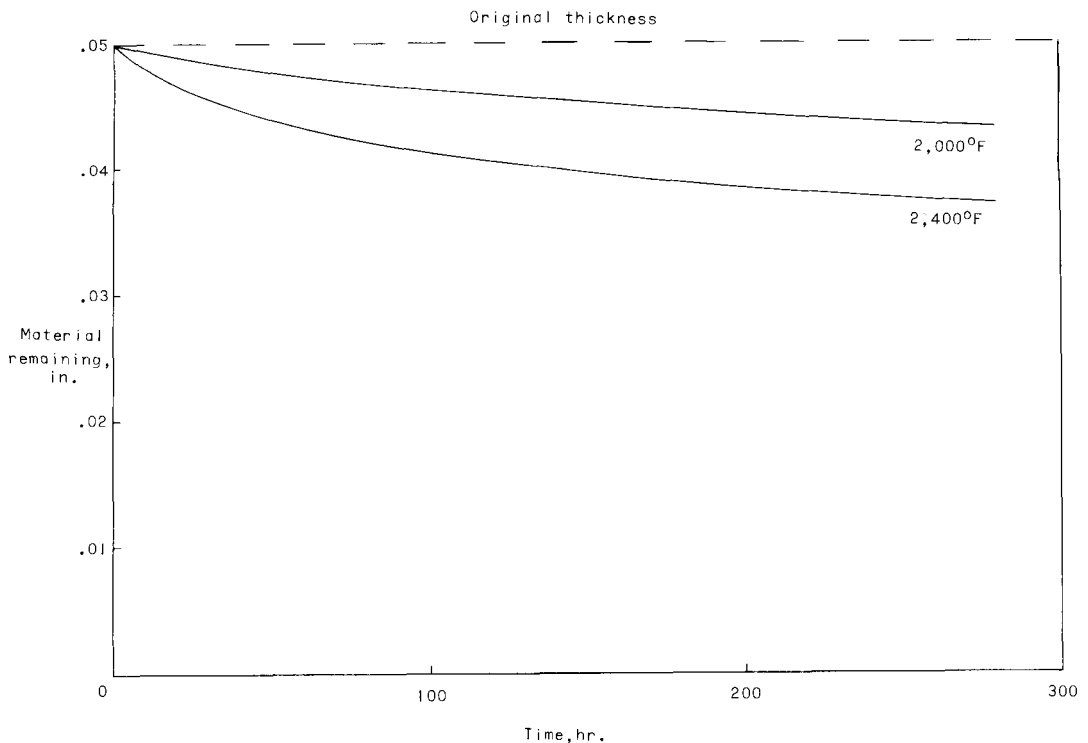


Figure 11.- Material remaining as a function of time for the thoriated-nickel sheet material at temperatures of 2,000° F and 2,400° F.

and 2,400° F. The material loss as shown by the curves is only 0.0050 inch in 285 hours at 2,000° F and 0.012 inch in 270 hours at 2,400° F.

Coated specimens.- The results of oxidation tests on coated sheet specimens are presented in figure 12. The figure shows curves of weight gained as a function of time at temperatures ranging from 2,000° F to 2,400° F. These results indicate there is negligible weight gained up to 2,200° F for many hours and very good resistance to oxidation for exposure times under 50 hours at 2,400° F. A complete study on intermetallic compounds formed in the coating and diffusion of

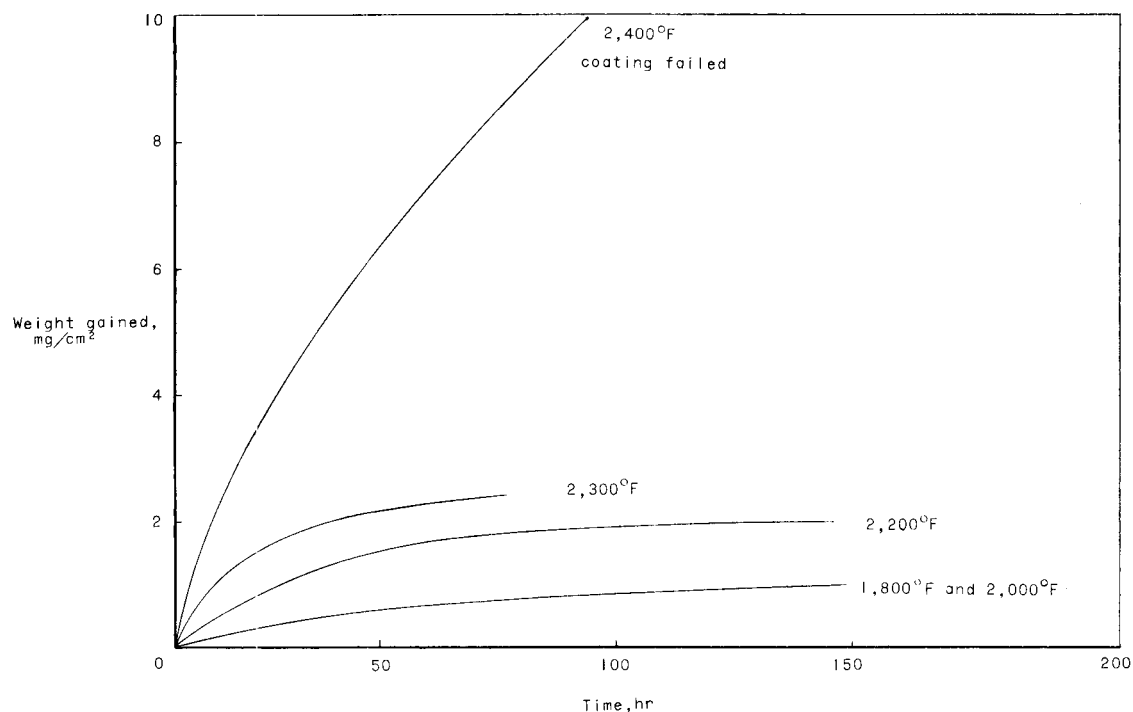


Figure 12.- Oxidation curves of the calorized thoriated-nickel sheet showing weight gained per unit area as a function of time.

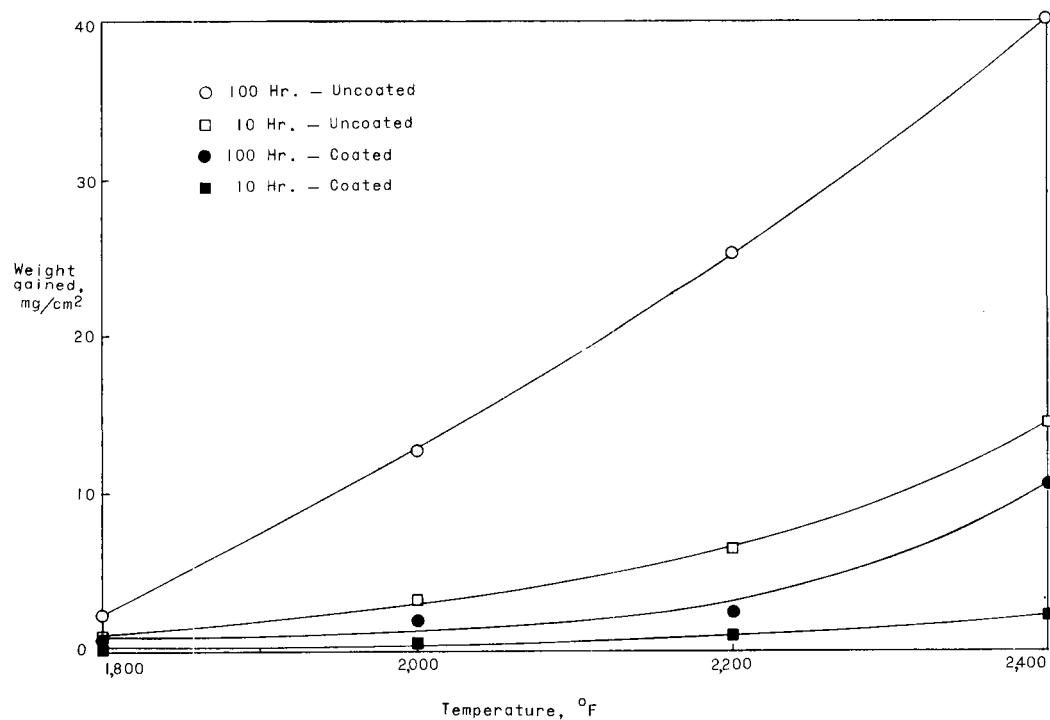


Figure 13.- Comparison of oxidation data for coated and uncoated thoriated-nickel sheet at 10 and 100 hours.

the coating into the base material will follow in a later section. These preliminary results on the calorized diffusion coating indicate that it protects the base material against oxidation for many hours at temperatures up to 2,300° F.

A comparison of the oxidation rates for coated and uncoated materials is given in figure 13. The weight gained per unit area is plotted as a function of temperature for 10- and 100-hour exposures, and the results indicate the coating reduces the oxidation considerably.

Metallurgical Investigation

X-ray investigation.- X-ray diffraction techniques were used to study the composition of the thoriated-nickel specimens in the following conditions: (1) as-received sheet, (2) sheet material with oxide film, (3) sheet material with diffusion coating, (4) and sheet material with diffusion coating after elevated-temperature exposure. The results of the X-ray diffraction measurements are presented in figures 14 and 15. The material in conditions 2, 3, and 4 was studied by running a diffraction pattern on the surface of the specimen, then removing material in increments of 0.0005 inch or more, and running successive diffraction patterns. This was continued until the diffraction pattern for the thoriated-nickel base material was again obtained.

The values of "d" spacings calculated from the diffraction record for the as-received uncoated thoriated-nickel material agree with the "d" spacings on the ASTM X-ray cards for Ni and ThO₂. This result indicates that only nickel and thoria are present. X-ray emission techniques were used to determine the amount of thoria in the oxide layer and in the calorized coating before and after exposure.

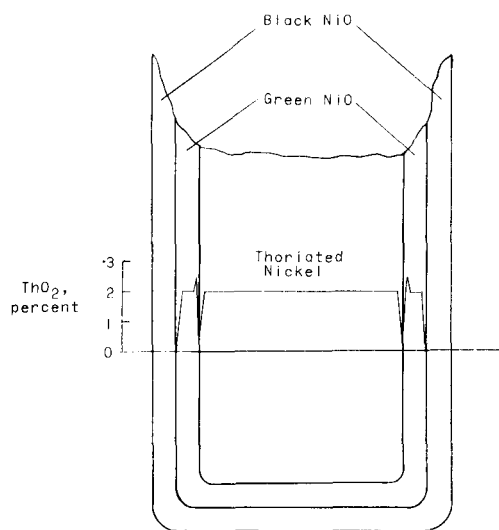
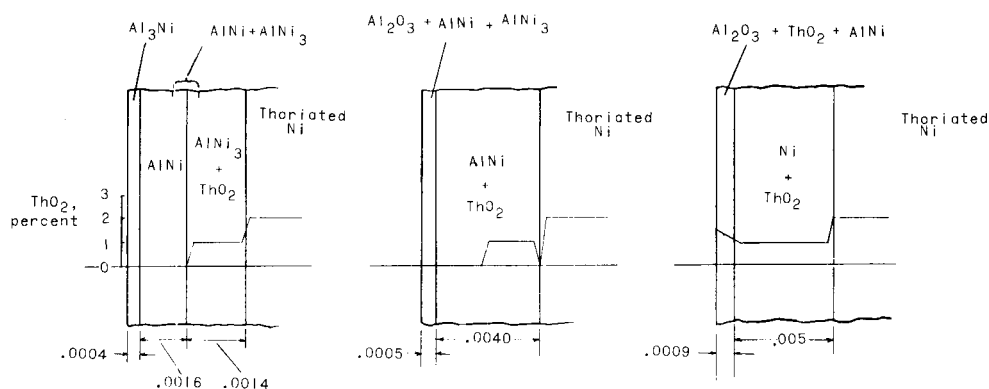


Figure 14.- Material composition and thoria distribution in the thoriated-nickel sheet after elevated-temperature exposure as shown by edge view.

Figure 14 gives the composition of the oxide film after elevated-temperature exposure. The X-ray analysis identified NiO in the black outer layer. The NiO, a stable oxide of nickel, has a cubic structure and melts at 3,050° F. There were two very strong reflections in the outer black layer (200) and (400) planes indicating that the oxide was preferentially oriented. After removing the black layer, a green layer was discovered. The X-ray pattern for the green layer was essentially the same as for the black layer, again indicating the presence of NiO. The only detectable difference noted in the X-ray data was, instead of two major reflections found in the black oxide, that there were reflections from eight lattice planes in the green layer. This result indicated that the green oxide layer was not preferentially oriented to the same extent. The X-ray

emission data obtained from the green oxide showed the ThO_2 increased from zero percent at the initiation of the green oxide to 2 percent. The percentage of thoria then tended to level off and remain at about 2 percent throughout the green oxide, but it again increased suddenly at the oxide-nickel interface to about 2.5 percent. Just beyond this interface a very thin thoria-depleted zone was detected in the thoriated-nickel material.

Both X-ray diffraction and X-ray emission analysis were employed to investigate the coating composition. The composition of the "as-deposited" coating is shown in figure 15(a) and after exposure at 2,000° F and 2,400° F in figures 15(b) and 15(c), respectively. The X-ray data show Al_3Ni on the surface with AlNi



(a) Zero exposure. (b) 50 hours at 2,000° F. (c) 45 hours at 2,400° F.

Figure 15.- Material composition and thoria distribution in the calorized thoriated-nickel sheet after elevated-temperature exposure shown by edge views.

directly below. A transition layer going from AlNi to AlNi_3 was noted. Below

this layer the major constituent was identified as AlNi_3 plus some thoria. The amount of thoria detected by emission studies appeared to be about 1 percent. The two aluminum-nickel intermetallic compounds (AlNi and AlNi_3) possess good oxidation resistance and excellent thermal stability. The AlNi melts above 3,000° F which exceeds the melting temperature of either Ni or Al. Figure 16 shows an electron-probe microanalyzer scan of the as-deposited coating supplied by Du Pont. It should be noted that there is excellent agreement between results of the coating composition found by the X-ray diffraction analysis and the electron-probe analysis.

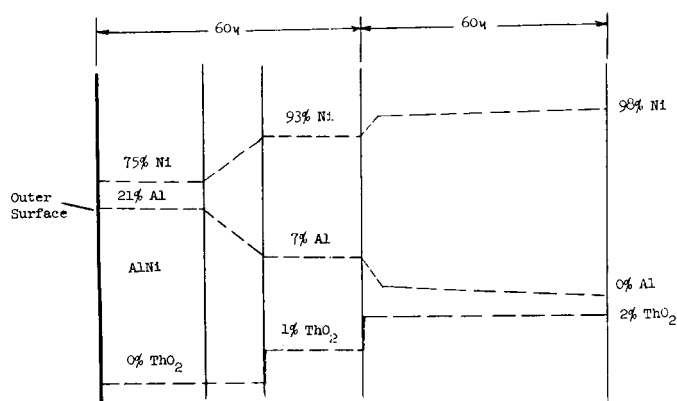
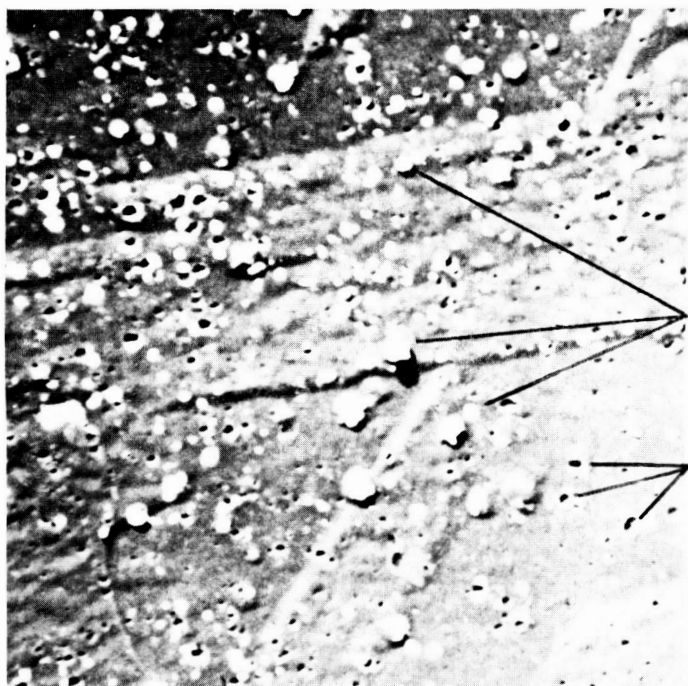


Figure 16.- Microprobe analysis of the as-deposited calorized coating on thoriated nickel. (Du Pont Co.)



(a) $\times 500$.



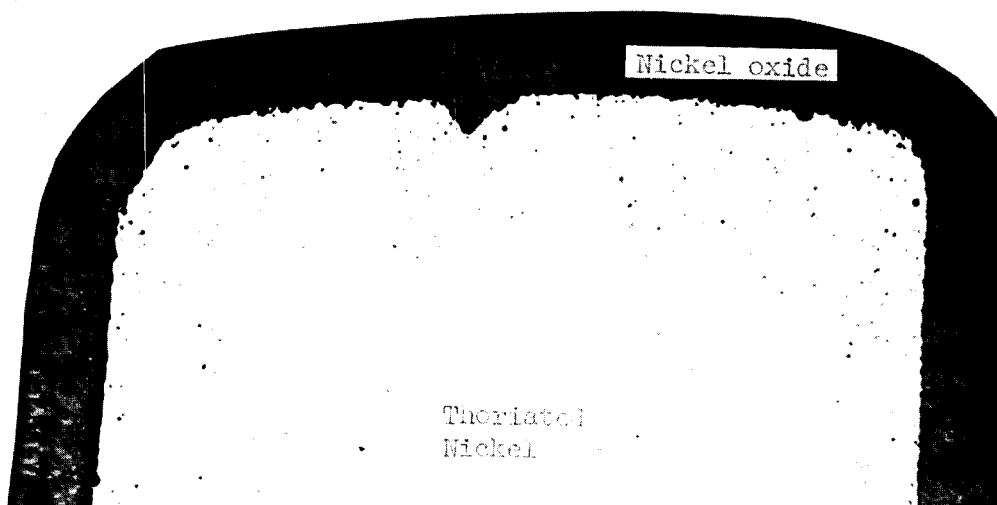
(b) $\times 10,000$.

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Figure 17.- Microstructure of as-received thoriated-nickel sheet.

The composition of the coating after exposure at $2,000^{\circ}\text{F}$ for 50 hours is shown in figure 15(b). The examination of the surface by X-ray diffraction indicated the presence of Al_2O_3 , AlNi , and AlNi_3 . Below the 0.0005-inch-thick surface layer, which contained all of the aforementioned constituents, the coating consisted almost entirely of AlNi . At a depth of 0.003 inch below the specimen surface the presence of thoria was detected and continued to the interface of the coating and the base metal where a thin layer appeared to be depleted of thoria. After exposure at $2,400^{\circ}\text{F}$ for 45 hours the composition was identified as shown in figure 15(c). The surface layer of Al_2O_3 increased in thickness with exposure time at elevated temperatures. The amount of AlNi and AlNi_3 in the surface layer decreased with exposure time until it was just barely detectable, but ThO_2 was readily detected on the surface and indicated that increased diffusion was taking place. Below the surface layer the material was identified as Ni with a small amount of ThO_2 . The ThO_2 increased to the normal 2 percent at the coating-metal interface.

Microstructure examination and diffusion study.- A study of the microstructure of the thoriated-nickel alloy was undertaken to determine the location of



(a) $\times 100$.



Thoriated
Nickel

(b) $\times 250$.

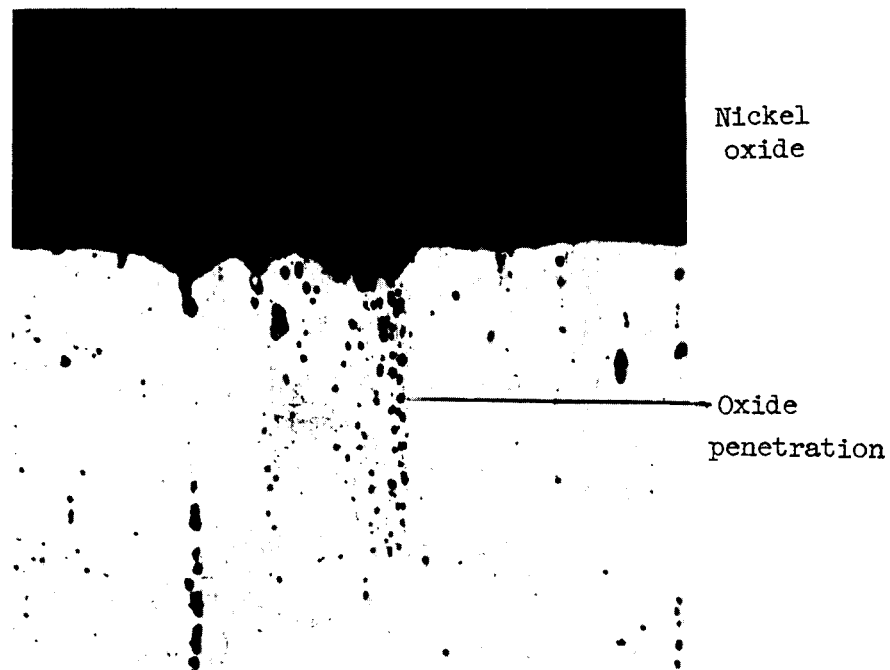
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Figure 18.- Microstructure of uncoated thoriated-nickel sheet after 168-hour exposure at 2,400° F.

the oxides, thoria particles, and intermetallic compounds found by X-ray diffraction analysis and to study possible coating diffusion during elevated-temperature exposure. Figure 17 shows the microstructure of thoriated nickel in the as-received condition. In figure 17(a) the thoria particles cannot be detected, but the electron micrograph (fig. 17(b)) shows thoria (black spots) and holes (light spots) where the thoria was removed during polishing. These thoria particles are submicron in size and were quite uniformly dispersed.

Photomicrographs of specimens after elevated-temperature exposure are shown in figures 18 to 20 and 22 to 24. Figure 21 shows the buildup in oxide film. The oxide film after exposures of 168 hours at 2,400° F is shown in figures 18. The film did not spall during rapid cooling which indicated that the oxide film is very adherent to the base-metal surface.

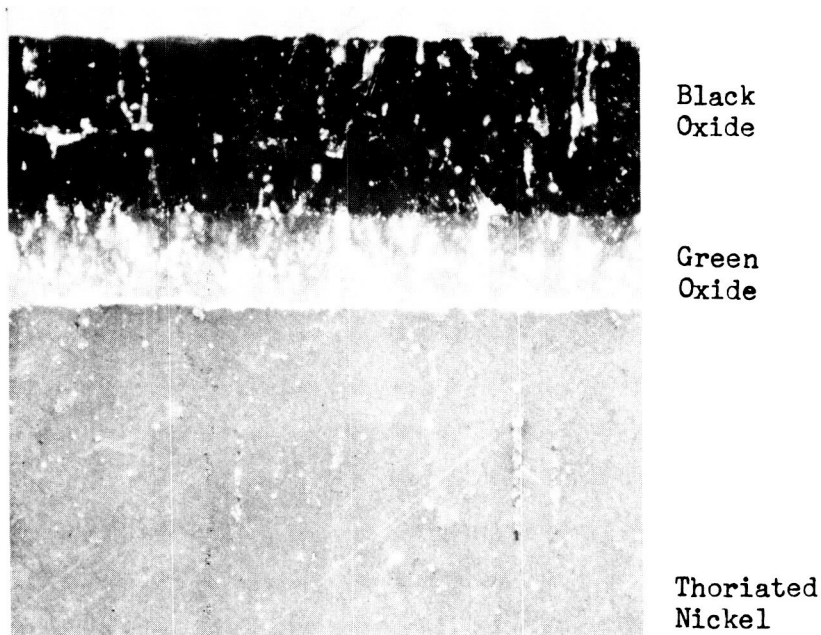
Figure 19 shows the oxide particles penetrating into the nickel matrix to some extent. A polarized light micrograph of the oxide film showing two distinct



L-63-3168

Figure 19.- Photomicrograph showing oxide penetration into the uncoated thoriated nickel after exposure for 24 hours at 2,400° F. × 250.

layers (black on outside and green on inside) is shown in figure 20. To study the formation of these differently colored NiO layers, a marker (0.001-inch platinum wire) was placed on the material surface before oxidation and then exposed for 250 hours at 2,400° F. The final position of the marker lay between the black and green oxide layer. This was also observed in reference 10. This position indicated that the original metal surface was very close to the position marked by the black-green oxide interface. If the thickness of the green oxide is added to the original material remaining after oxidation, the total is very close to the original sheet thickness. Therefore, it has been postulated that the black layer grows as a result of the diffusion of the nickel outward while the green oxide forms as a result of the diffusion of the oxygen inward. Oxidation studies (refs. 10 and 11) have shown that the black oxide is oxygen satisfied and that the mechanism controlling the rate of formation is the diffusion of Ni^{+2} ion along the vacant cation points of the oxide lattice. It is concluded from X-ray analysis (ref. 12) that the high-temperature oxidation of nickel is controlled by the oxygen diffusion from the intermediate points of the NiO lattice to the metal. This would account for the green oxide, in that the amount of oxygen present to form this would probably not be as plentiful as the amount available to form the black oxide. X-ray diffraction results (fig. 14) indicate that the stable thoria did not diffuse in the black oxide which gives further indication that the original metal interface was near the outer edge of the green oxide.



L-63-3169
 Figure 20.- Photomicrograph showing two distinct oxide layers after exposure of 180 hours at 2,200° F. Polarized light; $\times 500$.

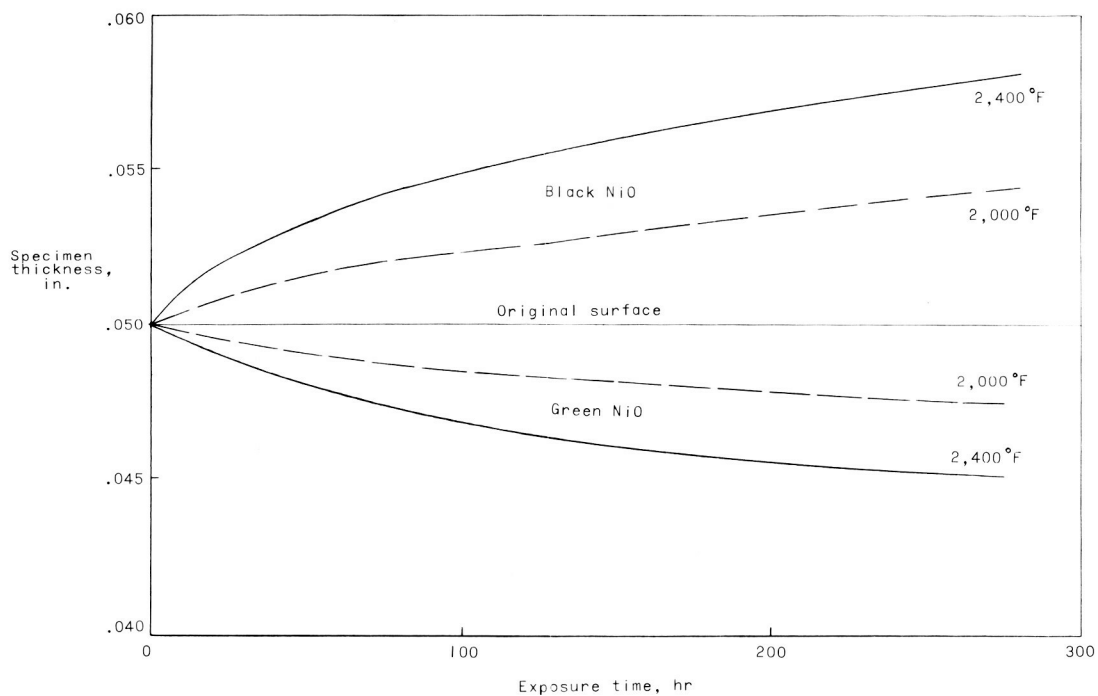
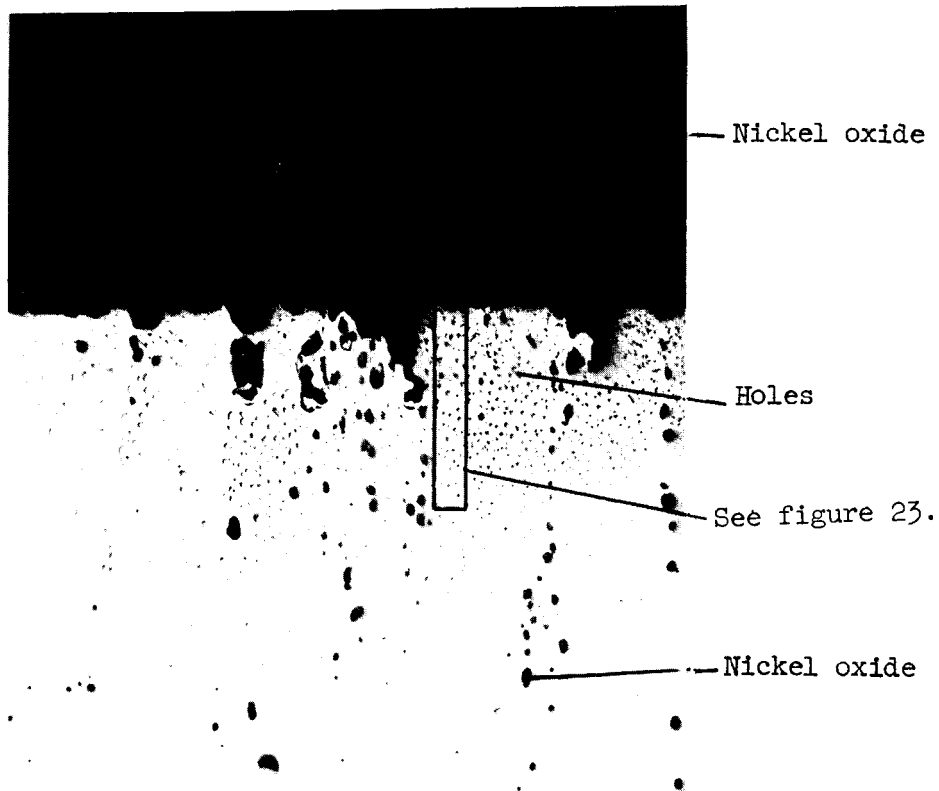


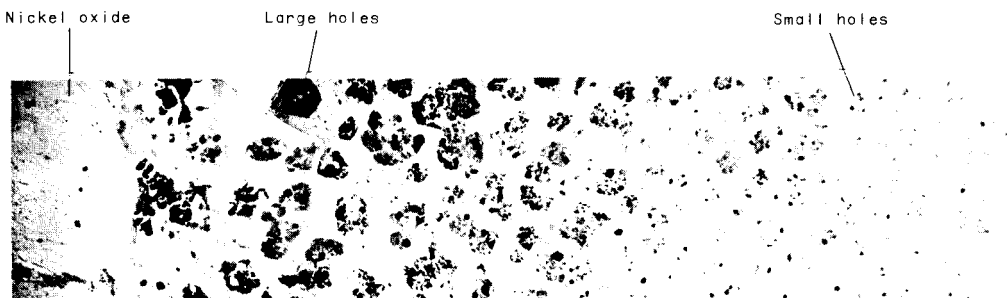
Figure 21.- Increase in oxide thickness as a function of time for thoriated nickel at 2,000° F and 2,400° F.

Figures 22 and 23 show small holes in the nickel matrix near the oxide innerface. These holes may account for the Ni that has diffused outward to form the black oxide. Figure 23 is a composite electron micrograph showing the oxide film (smooth) and the gradation of the holes from a large size near the oxide-metal innerface until they disappear in the nickel matrix.



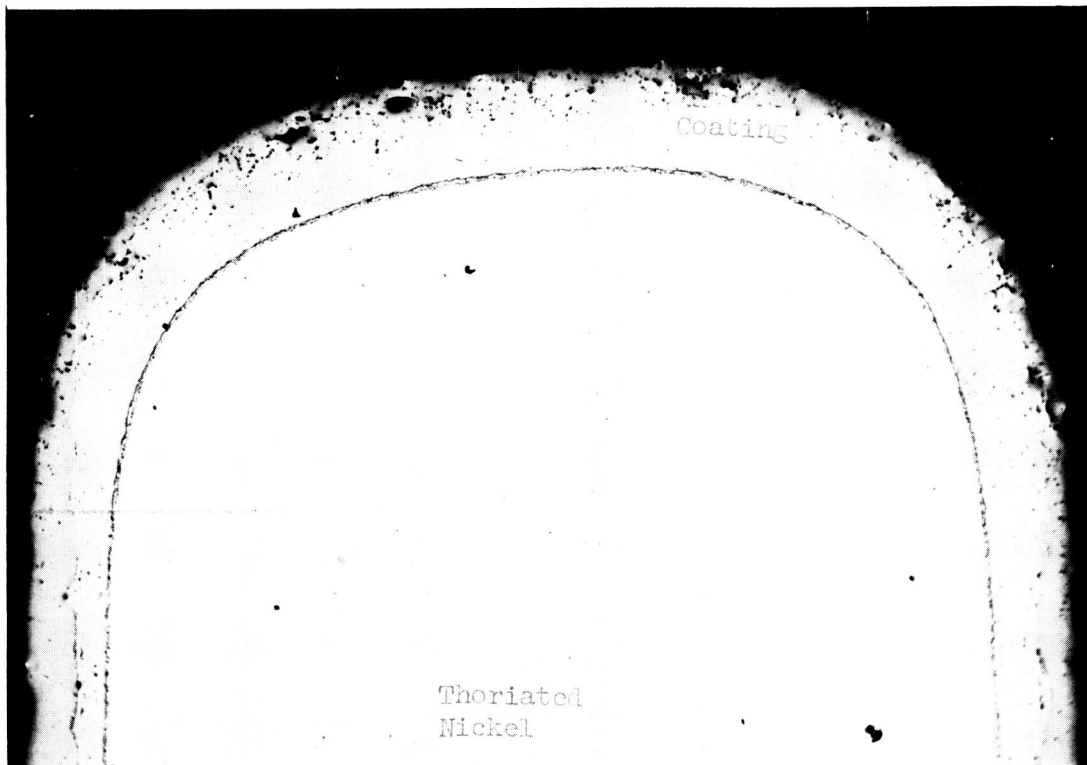
L-63-3170

Figure 22.- Microstructure of thoriated nickel after 100 hours at 2,200° F showing holes in the base material. $\times 250$.



L-63-3171

Figure 23.- Electronmicrograph of thoriated nickel showing gradation of holes in base material. $\times 3,000$.



L-63-3172

Figure 24.- Photomicrograph of a calorized thoriated-nickel sheet specimen showing coating uniformity on end. Edge view; $\times 100$.



L-63-3173

Figure 25.- Photomicrograph of as-deposited calorized coating showing individual grains. Polarized light; $\times 250$.

Micrographs of a coated and unexposed specimen are shown in figures 24 and 25. Figure 24 shows that the coating was applied uniformly and that no cracks are evident. In figure 25, the coating is shown at a higher magnification, and the individual grains in the coating are in evidence. The components in the coating were identified by X-ray diffraction (fig. 15) and were correlated with the microstructure study to provide the following interpretation. The thin surface layer contains a high percentage of aluminum (58 percent by weight) which is combined with the nickel to form Al_3Ni . The large columnar grains of AlNi form the second layer. A thin transition layer of AlNi plus AlNi_3 exists between the second and third layers. The third layer in which no individual grains are showing consists of thoria dispersed in AlNi_3 . Thus, it is seen that the diffusion of the aluminum inward and the nickel outward toward the surface occurs during the calorizing process. The innerface of the columnar grained AlNi and the AlNi_3 thoria phase is believed to be the sheet surface before calorizing because, thermodynamically, the thoria, as mentioned before, would not be expected to move. During application of the calorized coating, the Al diffused approximately 0.002 inch into the base material.

Figure 26 illustrates this effect of exposures at 50, 100, and 200 hours at $2,000^\circ\text{F}$ on the calorized specimens. The Knoop hardness values shown on the figures will be discussed in a subsequent section. The microstructure is correlated with X-ray diffraction results (fig. 15) to give the following interpretation. Aluminum from the Al_3Ni reacted with oxygen at the surface to form Al_2O_3 on the

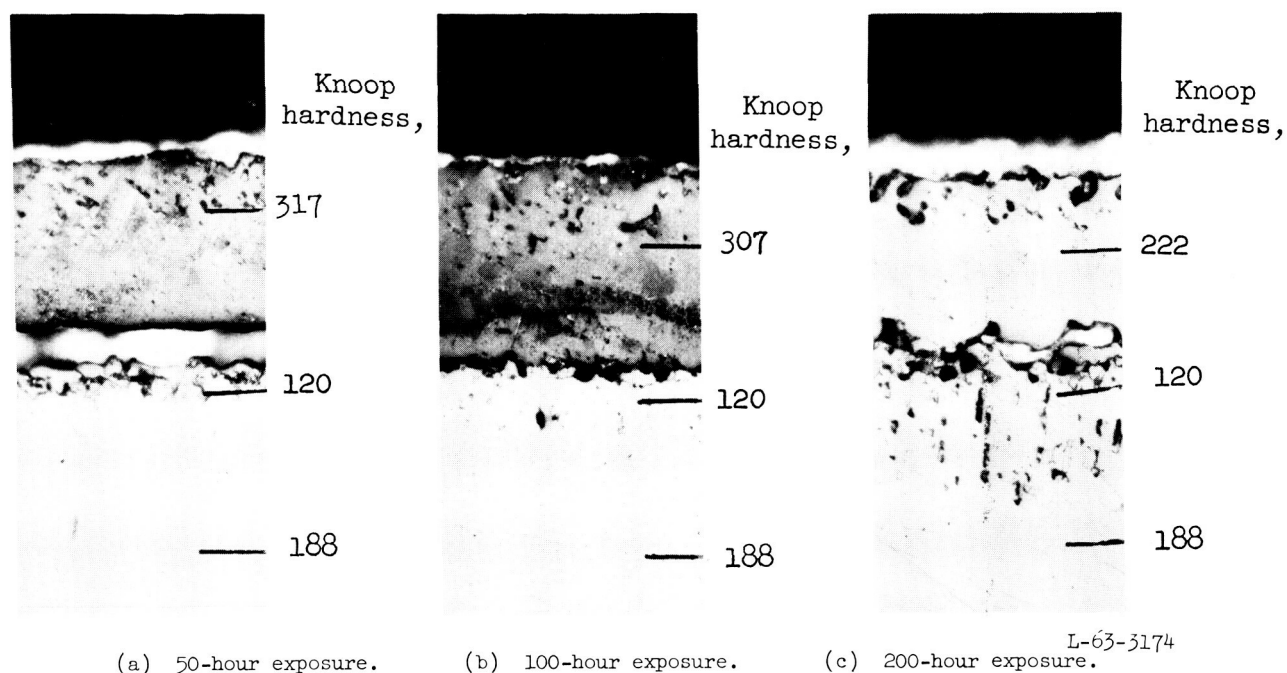


Figure 26.- Photomicrographs showing the effect of $2,000^\circ\text{F}$ exposure on the calorized coating for times up to 200 hours. $\times 250$.

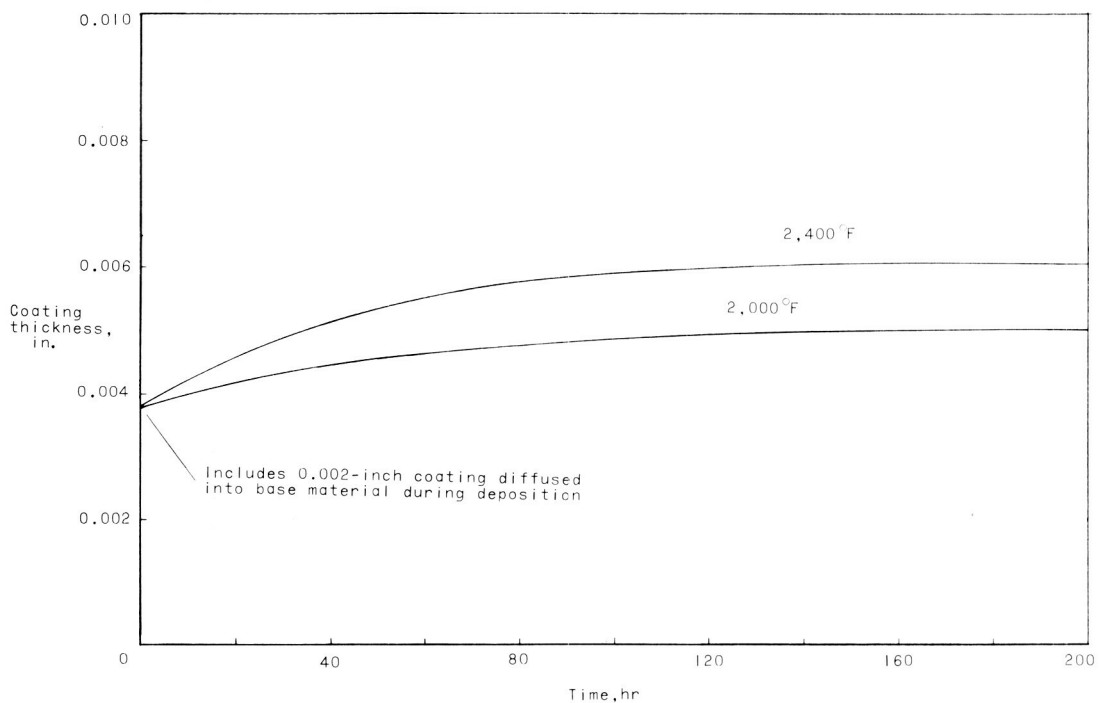


Figure 27.- Curves showing coating diffusion into base material at 2,000° F and 2,400° F.

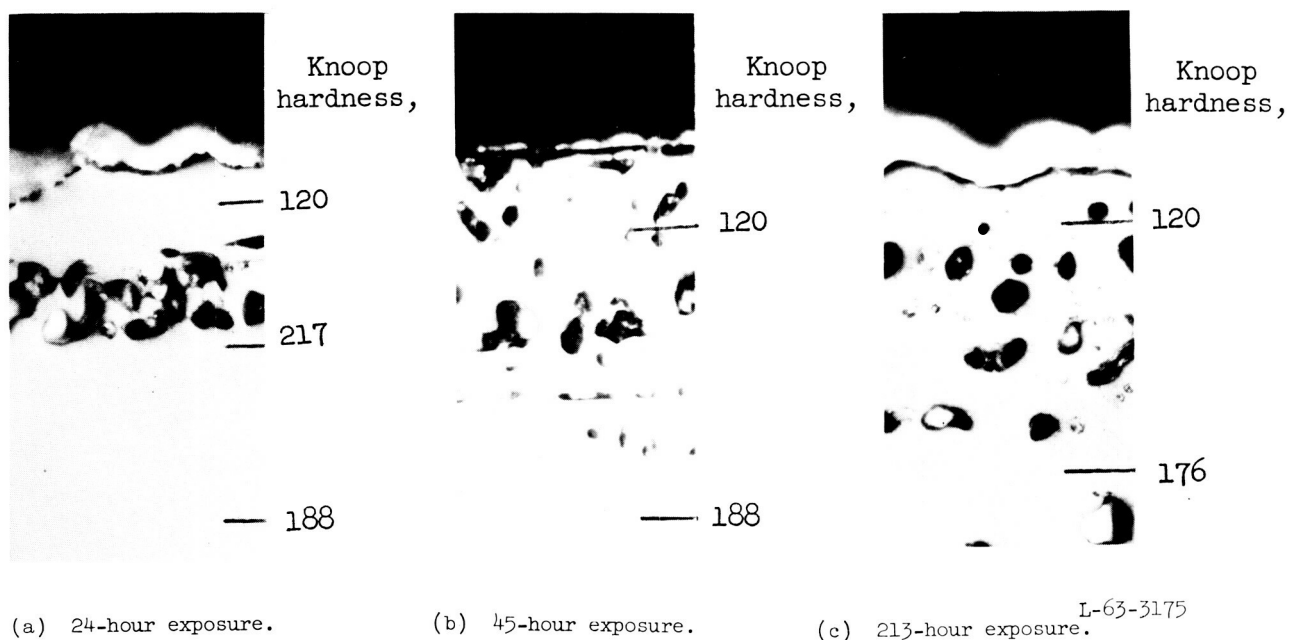
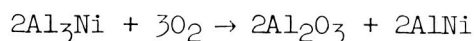


Figure 28.- Micrographs showing effect of 2,400° F exposure on the calorized coating for times up to 213 hours. $\times 250$.

surface and more AlNi intermetallic compound as follows:



At the same time aluminum was diffusing in toward the thoriated nickel forming more AlNi. It should also be noted that the AlNi grains are no longer visible as a distinct layer under the polarized light (fig. 26). The increase in coating thickness is plotted in figure 27 for the 2,000° F as well as for the 2,400° F exposures. The results of figure 27 indicate that the coating thickness remains relatively unchanged after an initial exposure time of 50 hours.

The effect of 24, 45, and 213 hours of exposure at 2,400° F on the coating is shown in figure 28 and the results are again correlated with the diffraction results (fig. 15). The aluminum in the coating is diffusing toward the surface to form a thick layer of Al₂O₃. The coating matrix at 2,400° F may be noted to look the same as the base material. In fact the coating was determined to be essentially pure nickel under the outside layer after exposures of 24 hours. This inside layer of the coating has many holes which may be due in part to the aluminum diffusing toward the surface.

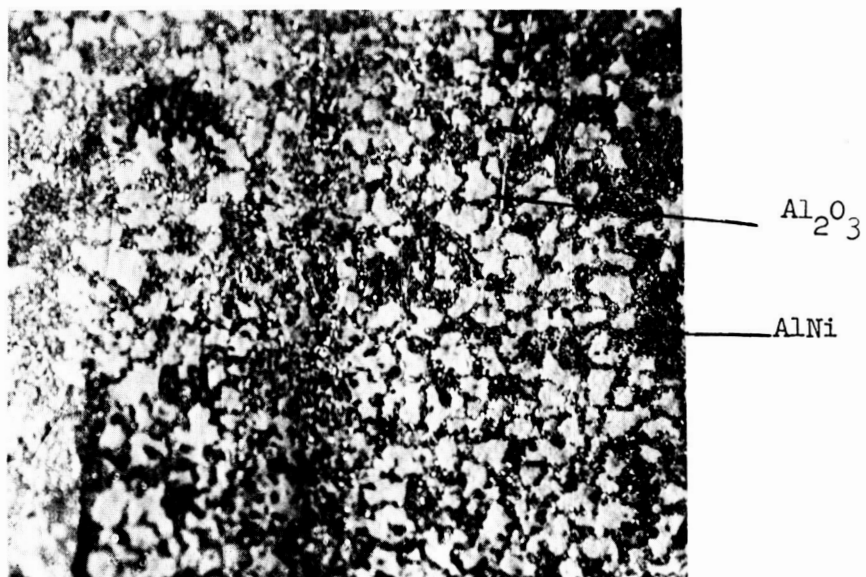


1/4 inch

L-63-1706

Figure 29.- Specimen showing bend ductility of diffusion coating after exposure at 1,800° F to 2,200° F.

A study of the coating ductility was also made, and tests revealed that the coating cracked if an attempt was made to bend the specimen before exposure. Figure 29 shows that the coating was ductile if bent after exposure at 1,800° F to 2,200° F. Bending after exposures at temperatures higher than 2,200° F caused coating failure. This may be explained from the results in figure 30 which shows the surface of the coating after exposure. The coating on figure 30(a) is made up of AlNi and Al₂O₃ with enough AlNi to allow bending without rupture after exposure at 2,200° F, but after exposure above this temperature the surface was almost entirely Al₂O₃ (fig. 30(b)) which cracked when bending was attempted. It appears that if the coating surface ruptured at 2,400° F,



(a) 75 hours at 2,200° F.



(b) 84 hours at 2,400° F.

L-63-3176

Figure 30.- Surface of the coated thoriated-nickel specimens after 2,200° F and 2,400° F exposures. $\times 12$.

the specimen would start to oxidize, but if the coating surface ruptured at 2,200° F and below, it would still resist oxidation as a result of the exposed stable AlNi.

The stability of the coating has been studied and the results indicate that it is very stable up to 2,200° F and possibly up to 2,300° F for 200 hours, but at 2,400° F it is not reliable at the present time beyond 50 hours although specimens have lasted as long as 213 hours at 2,400° F.

Hardness measurements.- Hardness measurements were made on specimens that had been calorized to study changes in the coating due to elevated-temperature exposure. The hardness values are tabulated on the photomicrographs in figures 25, 26, and 28. The hardness of the as-coated material (fig. 25) was 846 and 618 Knoop for AlNi and AlNi₃, respectively. The hardness on a thin section between the AlNi₃ and the base material was about 140 Knoop. This corresponds to a hardness value found in a piece of pure nickel which indicates an area of thoria depletion. The high hardness value of 846 in the AlNi is probably due to the compound being rich in Al. Reference 13 shows that an increase in hardness occurs in AlNi as a result of the vacancy-type defect structure found on the Al rich side of the compound. After exposure at 2,000° F, the hardness value of the AlNi dropped to 317. This drop can be accounted for by the diffusion of Al into the substrate from the AlNi which causes an enrichment in Ni. Reference 13 shows that as the AlNi compound reaches a 50-atomic-percent Al and 50-atomic-percent Ni state the hardness decreases to a minimum, and that the increase in hardness is much slower as the percentage of Ni rises. A thoria-depleted layer was again identified adjacent to the base material. After exposures at 2,400° F the basic coating area was very soft and had a hardness of 120 Knoop which is approximately the same as that for annealed nickel with no thoria. For the 24-hour exposure at 2,400° F, a thin layer with a hardness of 217 Knoop was found next to the thoriated nickel which indicates that some AlNi remained, but after 45 hours at 2,400° F all this AlNi disappeared and only Ni remained in the coating.

Fabrication

The fabrication characteristics were studied by machining high-temperature grips for creep-rupture testing, dimpling, and joining the thoriated-nickel sheet material by diffusion bonding, and tungsten-inert-gas (TIG), electron-beam, and resistance welding.

Machining.- The machined creep grips are shown in figure 31. The machining was accomplished with relative ease by using moderate cutting speeds and heavy feeds. The figure shows the surface of the grips after they have been calorized to resist oxidation.

Diffusion bonding.- A schematic drawing and a photograph of the diffusion-bonded sandwich panels are shown in figures 32 and 33. The panel on the left was constructed from 0.025-inch-thick sheet while the panel on the right was constructed from 0.0025-inch dimpled sheets, 0.004-inch-inside-face sheets, and 0.010-inch-outside-face sheets. The quality of the diffusion bond was checked by attempting to separate the face sheets from the dimpled center sheets. The

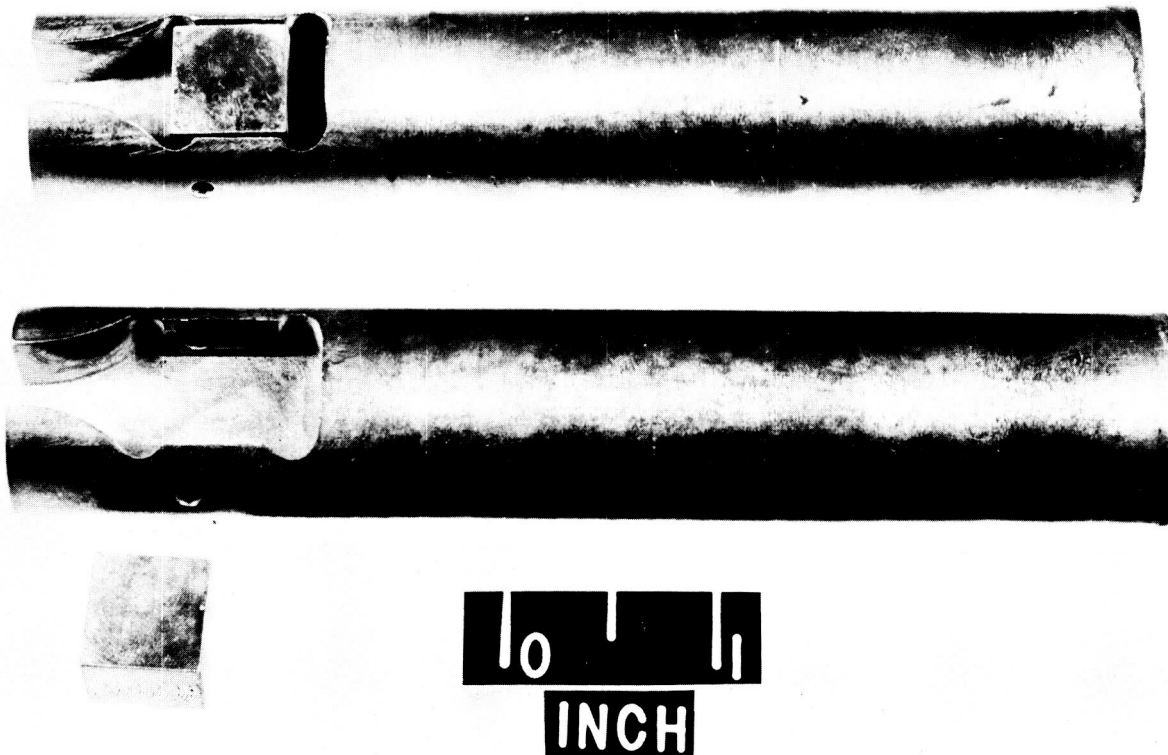


Figure 31.- Calorized thoriated-nickel tensile grips for use at elevated temperatures. L-63-4008

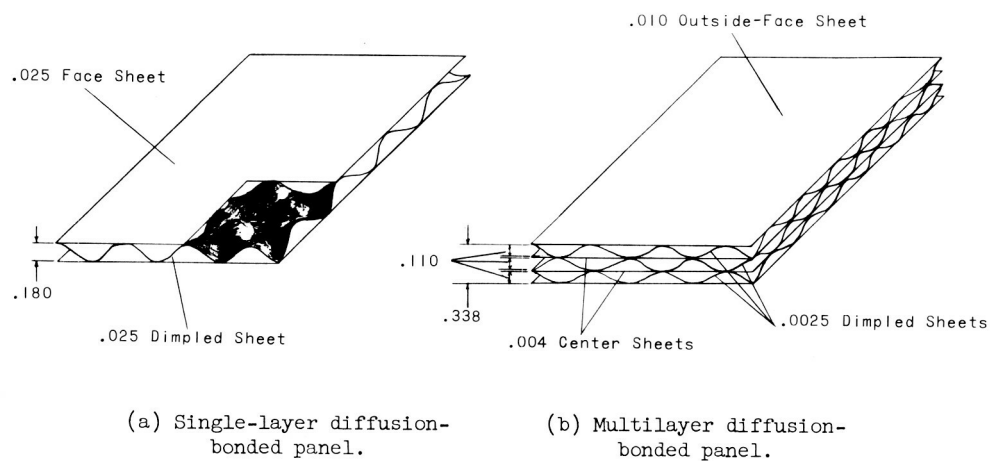
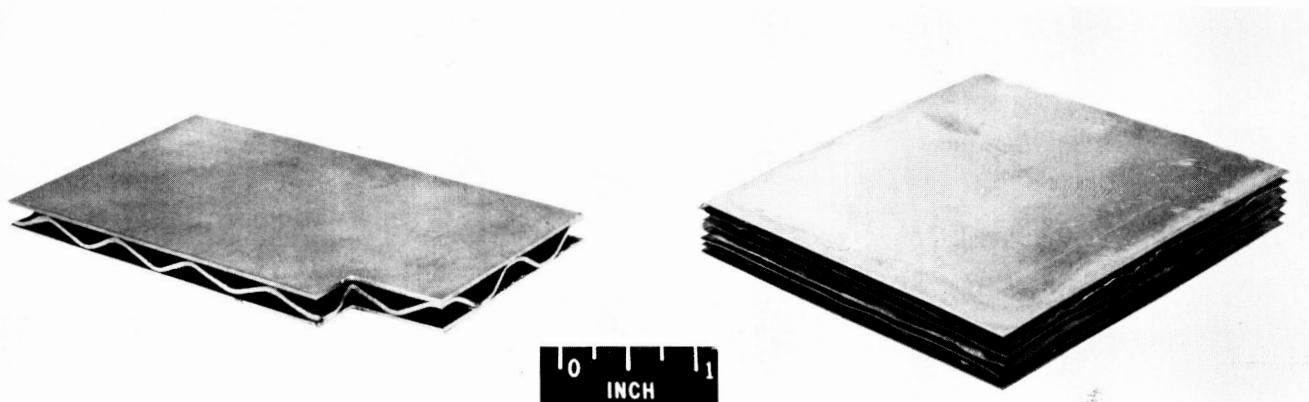


Figure 32.- Schematic of thoriated-nickel diffusion-bonded sandwich panels. All dimensions are in inches.

attempted separation resulted in pulling bonded plugs from the dimpled sheets which indicated the bond was stronger than the base material. A microsection was made of the bonded plugs (fig. 34) and it revealed no thoria agglomeration.



(a) Single-layer diffusion-bonded panel. L-63-705

(b) Multilayer diffusion-bonded panel. L-63-707

Figure 33.- Photographs of diffusion-bonded sandwich panels.



Figure 34.- Photomicrograph of diffusion-bonded thoriated-nickel sheets taken from a single-layer panel. $\times 500$. L-63-3177

Electron-beam welding.- Electron-beam welds were made on 0.025- and 0.050-inch-thick thoriated-nickel sheet. Welding parameters were determined and are given in table 4. The welds obtained were of good quality. Figure 35 shows a weld cross section on 0.025-inch-thick material. The figure shows there is some thoria agglomeration. It may be noted that the bend in the specimen was accomplished after welding, which indicates some ductility in the weld zone, although it did not show up in the elongation measurements over a 1-inch gage length after

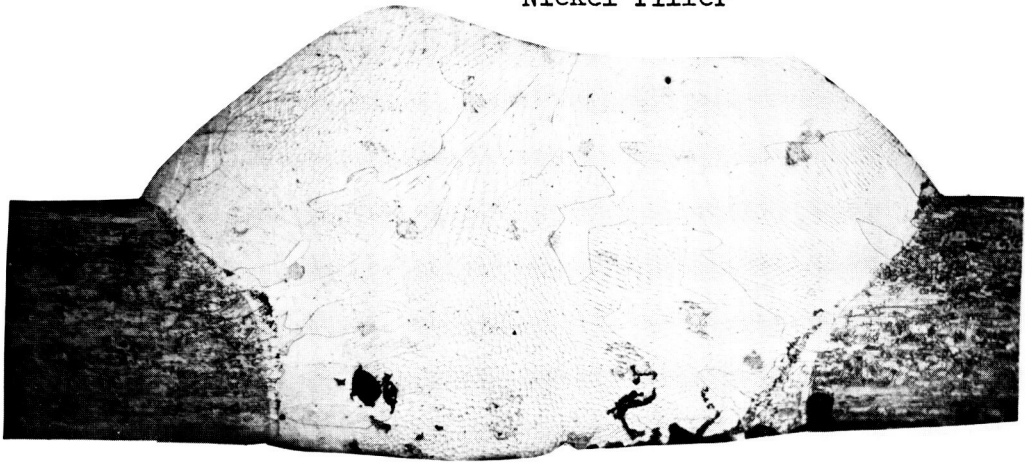
a tension test. This low elongation over the 1-inch gage length was accounted for by the observation that most of the deformation was taken up in the 1/8-inch-long weld zone. The weld strength was determined to be about 80 percent of normal room-temperature material strength.

Tungsten-inert-gas welding.- Tungsten-inert-gas (TIG) butt welds were made on thin sheet material. Welding methods were tried both with pure nickel filler rod and without filler rod. The welding parameters determined are given in table 5. Microstructures of butt-welded specimens using filler rod are shown in figure 36. Figure 36(a) shows the weld zone at low magnification. From this figure it is quite evident that the thoria has diffused into nickel filler. Figure 36(b) shows that the thoria particles agglomerated at the grain boundaries. Photomicrographs of TIG butt-welded specimens without filler rod are shown in figure 37. From the figure it may be noted that thoria agglomeration has again occurred. The strength of the welds using filler rod was found to be 80 percent of room-temperature material strength while the



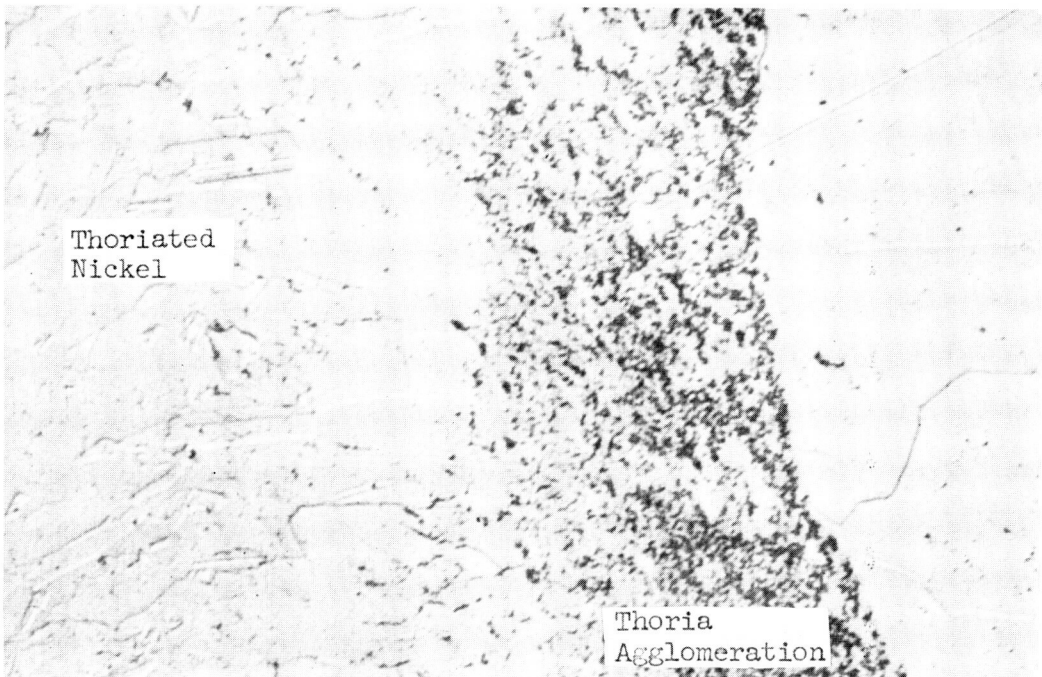
L-63-3178
Figure 35.- Electron-beam butt-welded 0.025-inch thoriated-nickel sheet material bent after welding to show weld ductility. $\times 150$.

Nickel filler



Thoriated
Nickel

(a) $\times 50$.



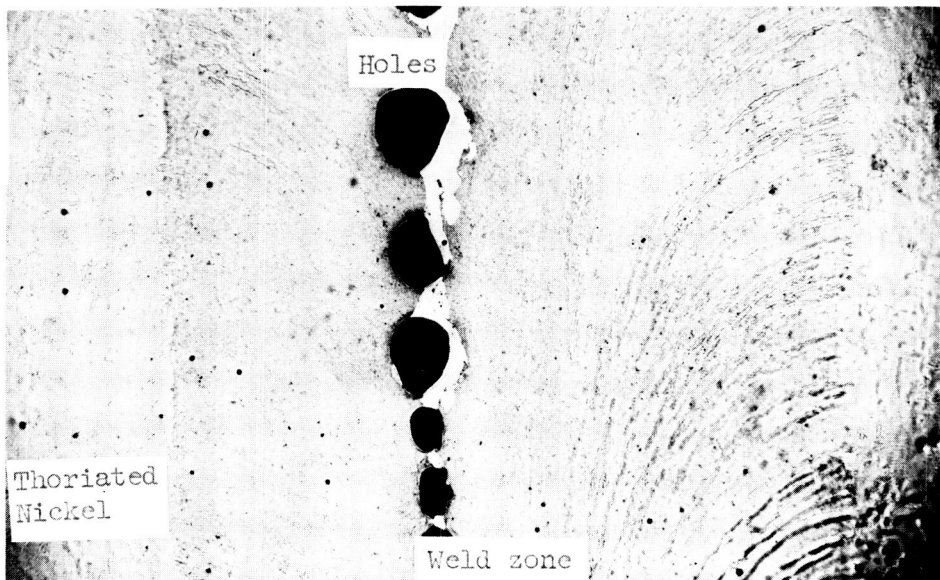
Thoriated
Nickel

Thoria
Agglomeration

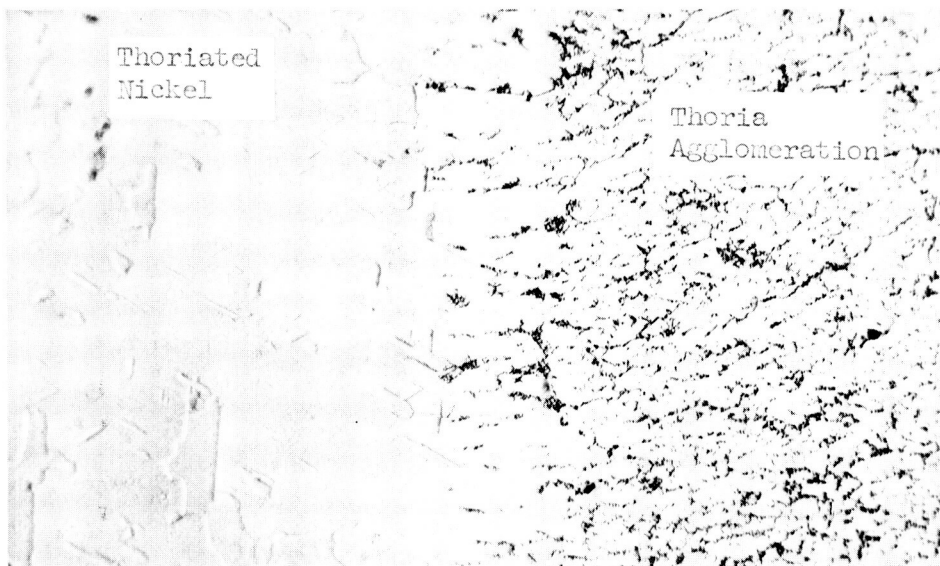
(b) $\times 800$.

L-63-3179

Figure 36.- Photomicrograph of tungsten-inert-gas butt-welded thoriated-nickel sheet using pure-nickel filler rod.



(a) $\times 25$.



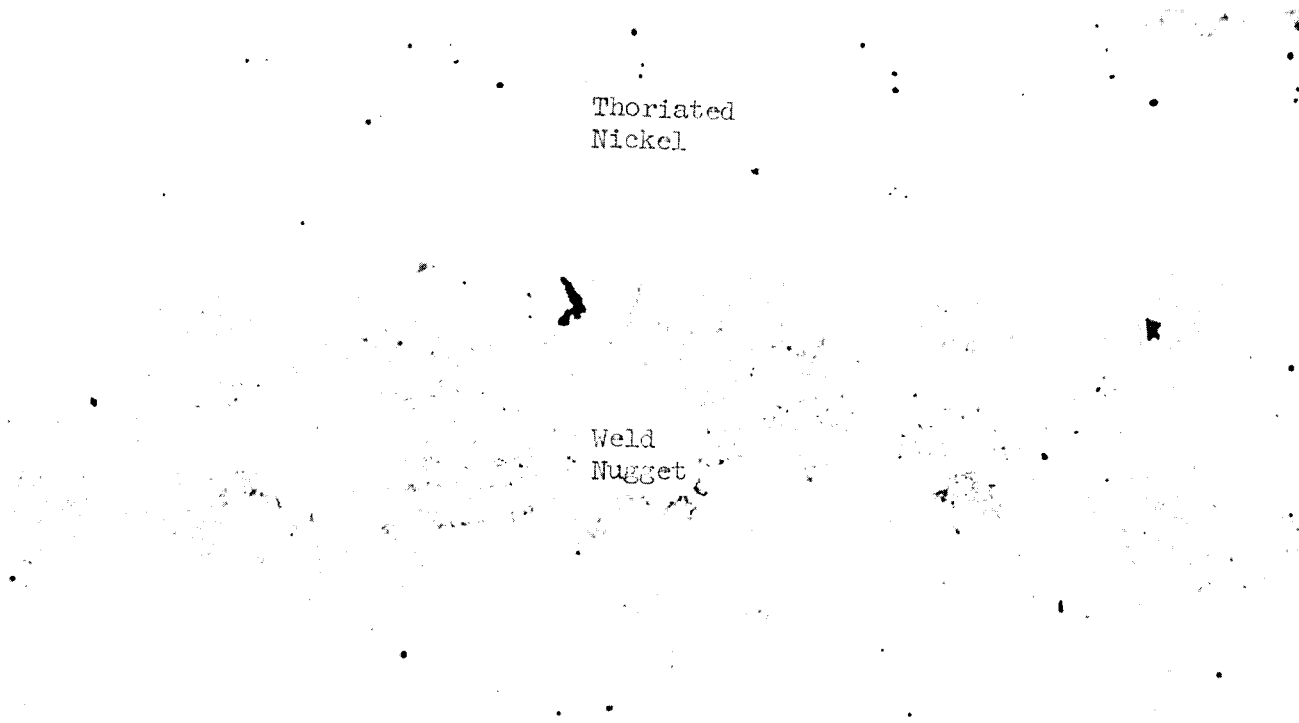
(b) $\times 500$.

L-63-3180

Figure 37.- Photomicrographs of a tungsten-inert-gas butt-welded thoriated-nickel sheet using no filler material.

strength of the welds using no filler was found to only be about 50 percent of the room-temperature material strength. This loss in strength was due to a weld porosity which is shown in figure 37. The elongation for TIG welded specimens without filler rod was found to be about the same as that for electron-beam welded specimens.

Resistance welding.- Thoriated-nickel sheets were joined by resistance-welding techniques. The parameters were determined and are given in table 6. After joining the sheets, a weld plug was pulled from one sheet and indicated that a very good weld had been made. The joined sheets were sectioned and are shown in figure 38. The figure shows a small amount of thoria agglomeration, but it is not as severe as noted during TIG welding.



L-63-3181

Figure 38.- Photomicrograph of a resistance weld in thoriated-nickel sheet. $\times 50$.

Examination of the sectioned electron-beam and TIG welds gave an indication that there was little sign of a heat-affected zone and no sign of grain-size increase in the thoriated-nickel base material. Some thoria agglomeration was noted in electron-beam-welded and TIG welded specimens where the nickel-base material had been melted. Therefore, joining techniques that do not cause appreciable melting of the material seem to be the most efficient joining methods for this material. No thoria agglomeration was noted in the diffusion-bonded sandwich and very little was noted in the resistance-welded material.

CONCLUSIONS

The results of this investigation indicate that the thoriated-nickel alloy should be considered for structural applications in aerospace vehicles in the temperature range from 1,800° F to 2,400° F. The material possesses good mechanical properties in this temperature range and has lower oxidation rates than uncoated refractory alloys. In addition, it may be coated by a commercial process to further reduce the oxidation rate and may be fabricated into complex configurations in thin gages by using standard equipment and tooling.

The following results are based on this investigation:

1. The room-temperature tensile tests revealed that thoriated nickel can withstand 2,000° F exposures for 24 hours with minor losses in strength. Calorized thoriated nickel can be exposed at temperatures to 2,200° F for times to 200 hours with small decreases in strength.
2. The elevated-temperature tensile tests on as-received material made at 1,700° F gave a tensile strength of 21.4 ksi. Further testing revealed that the material retains usable strength up to 2,500° F. A metallographic examination of tested specimens revealed that the thoria remained uniformly dispersed at 2,500° F.
3. The elongation decreased from 19 percent at room temperature to 3 percent at 2,570° F. Both coated and uncoated specimens that were exposed at elevated temperatures all showed room-temperature elongations of 8 percent or greater.
4. The oxidation rates of thoriated nickel were found to be higher than those of several other nickel-base alloys at 2,000° F, but the damage done to the material by oxidation was not as detrimental in thoriated nickel. A metallurgical examination showed a uniform surface attack on the thoriated nickel with no adverse effects on the grain boundaries, whereas the oxide attack on several precipitation-hardened nickel-base alloys such as René 41 was damaging to the grain boundaries which may reduce the usefulness of the material at these temperatures.
5. An aluminum diffusion coating applied to the material by the pack cementation method reduced oxidation at all temperatures from 1,800° F to 2,400° F. In fact the oxidation rates at temperatures to 2,200° F were reduced to a negligible amount. The coating was found not to be reliable at 2,400° F.
6. Fabrication studies of the material indicated that machining, forming, and joining could be accomplished with standard procedures. Joining studies revealed that resistance welding and diffusion bonding caused the smallest amount of thoria agglomeration. Tungsten-inert-gas and electron-beam welding indicated the thoria did agglomerate to a detrimental extent. The most satisfactory joining methods investigated appeared to be diffusion bonding and resistance welding.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., May 23, 1963.

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TABLE 1.-- TENSILE-TEST DATA FOR SHEET AT ROOM TEMPERATURE

Material condition	Sheet thickness, in.	Grain direction	Yield strength, psi	Ultimate strength, psi	Elongation in 1 inch, percent
As received	0.050	Longitudinal	62,500	85,400	19
As received	.050	Longitudinal	62,300	84,200	20
As received	.050	Transverse	55,000	78,400	23
As received	.050	Transverse	58,100	80,100	14
As received	.025	Transverse	52,200	79,950	19
As received	.025	Transverse	53,100	80,100	23
Oxidized at 2,000° F ^(a)	.050	Longitudinal	56,800	76,200	18
Oxidized at 2,000° F ^(a)	.050	Transverse	52,500	77,500	17
Oxidized at 2,400° F ^(a)	.050	Longitudinal	51,900	71,300	12
Calorized and unexposed	.050	Transverse	52,300	75,400	--
Calorized and exposed at 2,200° F ^(b)	.050	Longitudinal	45,000	76,100	14
Calorized and exposed at 2,400° F ^(c)	.050	Longitudinal	33,200	50,700	8

(a) Oxidized 24 hours.

(b) Exposed 192 hours.

(c) Exposed 88 hours, partial failure of coating.

TABLE 2.- TENSILE-TEST DATA FOR SHEET AT ELEVATED TEMPERATURES ON
AS-RECEIVED THORIATED-NICKEL ALLOY

Temperature, °F	Sheet thickness, in.	Grain direction	Yield strength, psi (a)	Ultimate strength, psi (b)	Elongation in 1 inch, percent
1,700	0.050	Transverse	17,400	21,400	5.0
1,800	.025	Longitudinal	15,500	20,100	4.0
2,000	.050	Longitudinal	14,700	17,800	5.0
2,050	.050	Transverse	13,850	16,800	4.0
2,100	.025	Transverse	12,500	15,000	3.5
2,400	.050	Transverse	5,400	7,300	3.5
2,480	.025	Transverse	4,000	6,000	2.0
2,500	.050	Longitudinal	3,850	5,200	3.0
2,570	.050	Transverse	2,400	4,100	3.0

(a) The yield point was taken as 0.002-inch offset.

(b) Specimens were held at temperature 1 minute before testing.

TABLE 3.- TENSILE-TEST DATA FOR ROOM-TEMPERATURE BUTT WELD

Weld type	Sheet thickness, in.	Yield strength, psi	Tensile strength, psi	Elongation in 1 inch, percent
Electron beam	0.025	47,500	55,800	2.0
Electron beam	.025	49,200	60,700	4.5
Electron beam	.050	48,800	58,200	3.0
Electron beam	.050	50,000	62,600	2.5
Electron beam	.050	49,500	60,000	2.0
TIG(a)	.025	50,700	64,500	4.5
TIG(a)	.025	52,300	68,200	6.5
TIG(a)	.025	52,700	68,000	6.0
TIG(a)	.050	52,200	68,500	4.5
TIG(a)	.050	53,800	72,000	6.5
TIG(a)	.050	46,500	58,000	7.0
TIG(b)	.050	40,100	40,600	2.0
TIG(b)	.050	41,700	43,800	2.0
TIG(b)	.050	43,900	45,000	2.0

(a) Nickel filler rod.

(b) No filler rod.

TABLE 4.- PARAMETERS FOR BUTT-WELDING SHEET MATERIAL BY
ELECTRON-BEAM TECHNIQUES

Parameter	0.050-inch sheet	0.025-inch sheet
Accelerating potential, kilovolts	13 ⁴	109
Beam current, ma	3	2
Welding rate, in./min	30	30
Beam deflection	0	0
Vacuum, mm Hg	10 ⁻⁴	10 ⁻⁴

TABLE 5.- PARAMETERS FOR BUTT-WELDING 0.050-INCH SHEET
MATERIAL BY TUNGSTEN-INERT-GAS METHODS

Machine type	National Cylinder Gas
Backup gas	Argon
Flow rate, cu ft/hr	5
Torch type	Hiliarc
Torch size	M50A
Electrode	3/32 thoriated tungsten
Shielding gas	Argon
Flow rate, cu ft/hr	30
Travel speed, in./min	5
Polarity	Direct current, straight polarity
Amperes	120
Arc volt setting	50
Stability setting	5

TABLE 6.- PARAMETERS FOR WELDING 0.050-INCH SHEET MATERIAL
BY RESISTANCE METHODS

Welding current, amp	27,000
Welding sequence	28 cycles (7 impulse, 4 heat, 2 cooling)
Pressure, lb	1,000
Wheel	Class I copper, 3-inch diameter